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THE

PHYSICAL REVIEW.

OSCILLATING SYSTEMS DAMPED BY RESISTANCE PROPORTIONAL TO THE SQUARE OF THE VELOCITY.

By J. Parker Van Zandt.

I. Introduction.

ALL bodies moving through a resisting medium encounter forces which affect their motion. In order to predetermine the motion of any dynamical system it is necessary to know the factors influencing the resisting forces and the laws governing their variations. The resistance may influence the motion very markedly; thus in the motion of large bodies at relatively high speeds, as in the propulsion of aëroplanes or of ships, the amount and variation of the resistance are dominant factors and determine the maximum velocity obtainable. A comprehensive study of the laws of damping is difficult because of the many variable factors influencing the forces of resistance. Since in many of the more important problems of engineering the predominant factor is velocity, we shall restrict the discussion to the variation of the forces of resistance with the velocity of the moving body. The resistance is considered as varying only with integral powers of the velocity, although experimentally it has been shown that the exponent of the resistance term is often fractional. . Such a restriction is necessary because it is extremely difficult if not impossible to treat mathematically the irrational expressions which would otherwise occur. From a practical standpoint, the introduction of irrational or fractional exponents is in most cases an unnecessary refinement because of the presence of other indeterminate factors, partially independent of the speed, which modify the damping.

It is sometimes assumed that the majority of forms of resisted motion fall into the class in which the opposing forces are directly proportional to the velocity. Many important engineering problems, however, involve resisting forces which are proportional to the square of the velocity. Thus in hydrodynamics the resistance to the motion of water in pipes,

conduits and surge towers, and the resistance to the motion of vessels, are approximately proportional to the square of the speed. When the resisting medium is air we have such problems as those of ballistics, of aërodynamics, of resistance to the motion of trains, and of air damping in some forms of electrical meters. One of the first to recognize the presence of the " square law " of resistance in the motion of projectiles through air was Sir Isaac Newton.[1] He observed the time of fall of spheres dropped from St. Paul's Cathedral and verified the law for moderate speeds. It has been found that for speeds approaching the velocity of sound, the effect of the elasticity of the fluid is felt and the index may rise considerably above its value when the resistance is a pure quadratic function. Comparing the results of German, Dutch, Russian and English experimenters, Cranz[2] has found that the index increases from 2 to 5 and then decreases to 1.55, as the speed of the projectile is increased up to and beyond the velocity of sound in air.

In aërodynamics the investigation of the laws of air resistance for large bodies moving at relatively high speeds has been for several years one of the chief occupations of aëronautical research. Zahm,[3] Lanchester[4] and others have studied the problem and find two factors, one called the head resistance, which varies with the square of the velocity within certain limits, and a second form of resistance, caused by surface friction, which varies with the 1.86 power of the velocity. It is of interest to electrical engineers to know that formerly some of the electrical supply meters depended for their operation upon the motion of fans in air or liquids, which caused resisting forces varying with the square of the speed. Such were the Forbes, the Schallenberger, the Ferranti and the Slattery meters.[5] A close similarity exists between the action of the retarding forces in air and in water. It has been shown experimentally that the exponent for surface friction when water flows through pipes and channels is 1.85; this is almost exactly the value given by Zahm for the resistance of the air when flat or tapering bodies move edgewise. If the flow of the water is turbulent the index rises to the square,[6] corresponding thus to the expression for the resistance met by blunt bodies propelled through air. In viscous fluids, Stokes's law of resistance varying with the first

[1] Sir Isaac Newton, Principia, Book II., Sec. VII.

[2] Cranz, "Ballistik," Encykl. der math. Wissenschaften, Vol. IV., Part 2, 1903. Contains a complete bibliography. See also Encycl. Brit., Ballistics.

[3] Zahm, Philosoph. Soc. Washington, 1904.

[4] Lanchester, Aërial Flight, Vol. I., Chap. 2, 1908; A discussion concerning the Theory of Sustentation and Expenditure of Power in Flight, Eng. Cong., San Francisco, 1915; Berriman, The "Arrival" of the Aëroplane, Eng. Cong., San Francisco, 1915.

[5] Swinburne, The Measurement of Electrical Currents, 1893; Parr, Electrical Engineering Measuring Instruments, 1903.

[6] Knibbs, Proc. Roy. Soc. N.S.W., Vol. 31, 1897.

power of the velocity, based on the assumption of non-sinuous motion with no slipping at the boundary, was found by Allen[1] to hold for the motion of bubbles and small solid spheres in liquids if the velocity remained small, but if the velocity was increased sufficiently the resistance approximated the square law closely.

An interesting problem in hydraulic engineering appears in the design of surge towers to regulate the oscillations occurring in long conduits when the rate of flow is suddenly varied. If the flow is shut off entirely, the surges arising between the tower and the adjoining conduit represent in effect a freely oscillating system damped by resistance approximately proportional to the square of the velocity. In most of the papers listed below[2] a graphical or step-by-step method of integration is presented; in some the resistance is assumed to vary with the first power of the velocity; in none is a strictly analytical solution given for the oscillations when the resistance is assumed proportional to the square of the velocity. The resistance to the motion of vessels has been found to be similar to that discussed in the paragraph on aërodynamics. The head resistance varies with the square of the speed while the frictional resistance is proportional to a somewhat lower index. For the case of a ship rolling in still water White[3] assumed the resistance to vary partly as the angular velocity and partly as the square of the angular velocity. When rolling among waves the motion of the ship becomes a forced oscillation with a periodic forcing cause and damped by resistance varying with both the first and second powers of the angular velocity.[4]

This brief discussion is in no sense complete; it is intended merely to suggest the wide scope and prevalence of the square law of damping, and to indicate certain problems involving oscillating systems which are presented for solution.

II. Free Oscillations Damped by Resistance Proportional to the Square of the Velocity.

The equation of motion for a system executing free oscillations and opposed only by a force varying as the square of the velocity is

[1] Allen, Phil. Mag., Ser. 5, Vol. 50, 1900, pp. 323 and 519.

[2] Johnson, The Surge Tank in Water Power Plants, Trans. Am. Soc. Mech. Eng., Vol. 30, p. 443, 1908; Uhl, Speed Regulation in Hydro-Electric Plants, ibid., Vol. 34, p. 379; 1912; Durand, On the Control of Surges in Water Conduits, ibid., Vol. 34, p. 319, 1912; Warren, Penstock and Surge Tank Problems, Proc. Am. Soc. Civ. Eng., Vol. 40, 2, p. 2521, 1914; Church, Surge in a Hydraulic Stand Pipe, Cornell Civ. Eng., Dec., 1911; Forcheimer, Zeitschr. d. Ver. Deutsch. Ing., Vol. 56, p. 1291, 1912 (includes a bibliography of the foreign literature); Prasil, Surge Tank Problems, The Canadian Eng., 1914 (includes a bibliography).

[3] Sir Wm. H. White, Trans. Inst. Nav. Arch., 1895.

[4] Sir Philip Watts, Shipbuilding, Ency. Brit., 1910. See also Henderson, Engineering, April 18, 1913.

$$\frac{d^2\theta}{dt^2} \pm N\left(\frac{d\theta}{dt}\right)^2 + M\theta = 0. \tag{1}$$

Poisson[1] and others have investigated this equation for small oscillations, considering the higher powers of the successive arcs as negligible. Routh[2] performs the first integration and obtains a relation between the velocity and the displacement. Grammel[3] and Ignatowsky[4] give approximate solutions showing the displacement in terms of the time, useful when the oscillations are small but not adapted to larger values of the displacement. In the following pages a solution is developed which is particularly adapted to large displacements and heavy damping. In addition an experimental method is presented, by which it has been found possible to verify the results of the analytical study.

Transforming equation (1) by means of the proper substitutions and performing the first integration, the expression for the velocity in terms of the displacement is

$$\left(\frac{d\theta}{dt}\right)^2 = \frac{M}{2N^2} \mp \frac{M}{N}\theta + C_1\epsilon^{\mp 2N\theta}, \tag{2}$$

wherein C_1 is the constant of integration and depends on initial conditions. In order to define the meaning of the remaining symbols let us consider the motion of a torsion pendulum to be thus expressed. Then θ is the angle of displacement from the position of equilibrium; M is the restoring torque in cm.-dynes per radian of twist, divided by the moment of inertia of the pendulum about the axis of support; N is the coefficient of resistance, that is, the torque per square of unit angular velocity divided by the moment of inertia. The double sign before N is necessary because a change in the direction of the motion does not automatically change the sign of the resistance term. At each turning point, therefore, a discontinuity is introduced into the equation.

The integral of equation (2) expresses the relation between the angle of displacement θ and the time T.

$$\int dt = \pm \int \frac{d\theta}{\left(\frac{M}{2N^2} \mp \frac{M}{N}\theta + C_1\epsilon^{\mp 2N\theta}\right)^{1/2}}. \tag{3}$$

It is not possible to integrate the right-hand member of equation (3) in the form as written. For certain restricted values of N and θ, however, it is possible to express this integral in terms of a converging series and

[1] S. D. Poisson, A Treatise of Mechanics, Vol. I., Sec. 186–190.

[2] E. J. Routh, Dynamics of a Particle, Art. 129, 1898.

[3] R. Grammel, Physik. Zeitschr., Vol. 14, p. 20, 1913.

[4] W. v. Ignatowsky, Archiv. d. Math. u. Phys., Vol. 17, p. 338, 1910.

thus to obtain a relation between θ and the time. Substituting $z = (1 \mp 2N\theta)$ and assuming as initial conditions $\theta = \theta_0$ and $d\theta/dt = 0$ when $T = 0$, in order to determine C_1, equation (3) becomes

$$T - C = -\frac{1}{\sqrt{2M}} \int [z]^{-1/2} \left[1 - \left(\frac{z_0}{e^{z_0}} \right) \frac{\epsilon^z}{z} \right]^{-1/2} dz. \tag{4}$$

C is the constant resulting from the second integration and z_0 is the value of z at $T = 0$. The upper sign in the expressed value of z corresponds with positive angular velocity, the lower sign with negative angular velocity. If the absolute value of $(z_0\epsilon^z/\epsilon^{z_0}z)$ is less than unity, the right-hand member of equation (4) may be expanded according to the binomial theorem into an infinite series which converges absolutely. Assuming for the moment that the values of N and θ are such that this expansion is permissible,

$$\begin{aligned} T - C = -\sqrt{\frac{2}{M}} \int \Big[1 + \tfrac{1}{2}k \frac{\epsilon^{y^2}}{y^2} + \tfrac{3}{8}k^2 \frac{\epsilon^{2y^2}}{y^4} + \tfrac{5}{16}k^3 \frac{\epsilon^{3y^2}}{y^6} + \cdots \\ \cdots + \frac{(-\frac{1}{2})(-\frac{1}{2}-1)\cdots(-\frac{1}{2}-n+1)}{n!}(-k)^n \frac{\epsilon^{ny^2}}{y^{2n}} + \cdots \Big] dy, \end{aligned} \tag{5}$$

where $k = z_0/\epsilon^{z_0}$ and $z = y^2$. The integration of the series, equation (5), may be expressed as the sum of the integrals taken term by term. The general integral is

$$a_n \int \frac{\epsilon^{ny^2}}{y^{2n}} dy = a_n \int \frac{1}{y^{2n}} \left[1 + ny^2 + \frac{n^2y^4}{2!} + \frac{n^3y^6}{3!} + \cdots \right] dy. \tag{6}$$

For values of $z_0\epsilon^z/\epsilon^{z_0}z$ less than 0.99 it is sufficient for most purposes to consider the first six terms of the binomial expansion, equation (5), and the first seven terms of the expansion of each integral. The result is the following equation expressing the time T in terms of the displacement θ.

$$\begin{aligned} T - C = -\sqrt{\frac{2}{M}} \Big[\Big((1+\alpha)y + \frac{\beta}{3}y^3 + \frac{\gamma}{5}y^5 + \frac{\delta}{7}y^7 + \frac{\zeta}{9}y^9 + \frac{\eta}{11}y^{11} \Big) \\ - \Big(\frac{\alpha}{y} + \frac{\lambda}{3y^3} + \frac{\mu}{5y^5} + \frac{\nu}{7y^7} + \frac{\rho}{9y^9} \Big) \Big], \end{aligned} \tag{7}$$

where $y = \sqrt{z} = \sqrt{1 \mp 2N\theta}$. The constants $(\alpha, \beta, \gamma, \delta, \zeta, \cdots)$ are found by collecting the coefficients of the terms in like powers of y obtained from the expansion of each member of equation (5). A simple relation connects each constant with the preceding constant. All of the terms in the right-hand member of (7) are known when the constants N and M are specified and the desired value of θ is chosen. We have therefore a complete solution of the differential equation (1), subject only to the limitation

in the values of N and θ necessary to make the expansion absolutely convergent.

If $z_0\epsilon^z/\epsilon^{z_0}z$ is greater than unity equation (4) may be written

$$T - C = -\frac{1}{\sqrt{2M}}\int [-k\epsilon^z]^{-1/2}\left[1 - \left(\frac{\epsilon^{z_0}}{z_0}\frac{z}{\epsilon^z}\right)\right]^{-1/2} dz. \qquad (8)$$

This expresses the product of two absolutely convergent series. It may therefore be developed by the method outlined above and a second solution for T found, in terms of the displacement θ. This solution will be applicable for all values of N and θ for which (7) is not valid, save for the unique case $z_0\epsilon^z/\epsilon^{z_0}z = +1$ which renders both forms of solution indeterminate. It will be noted that at $T = 0$, $z = z_0$ and the solution assumes the indeterminate form. Hence it is necessary to know the value of T for any one angle θ other than θ_0, say the value of T when $\theta = 0$ and the vibrating system is passing through the position of equilibrium. At this value the series converges very rapidly. The constant of integration may be derived as well from the value of T at the first turning point, but here the expression (7) is in general less rapidly convergent.

We have in equations (7) and (8) relations by which the value of the displacement may be found at any instant. It is often desirable and sufficient for the purpose at hand to find merely the value of θ at the turning points. This may be done by placing $d\theta/dt = 0$ in equation (2) and determining C_1 from the condition that $\theta = \theta_0$ when $T = 0$. Then if θ_1 is the displacement at the first turning point,

$$(1 \mp 2N\theta_1)\epsilon^{\pm 2N\theta_1} = (1 \mp 2N\theta_0)\epsilon^{\pm 2N\theta_0} \equiv A. \qquad (9)$$

Expanding $\epsilon^{\pm 2N\theta_1}$ into an infinite series which converges absolutely for all values of $\pm 2N\theta_1$, equation (9) may be reduced to the following form:

$$2N\theta_1 = \sqrt{\frac{1 - A}{.5 + X}}, \qquad (10)$$

where

$$X = \frac{2N/\theta_1/}{3} + \frac{(2N\theta_1)^2}{8} + \frac{(2N/\theta_1/)^3}{30} + \frac{(2N\theta_1)^4}{144} + \cdots. \qquad (11)$$

All of the terms in X are additive, even when the angle θ_1 is negative; it is a rapidly converging series, especially when $2N/\theta_1/$ is less than unity. In general $2N/\theta_1/$ is considerably less than unity so that the equation presents a practical form for finding θ_1 by successive approximations. It appears also from equation (10) that the ratio of successive arcs is independent of the magnitude of the restoring torque M, contrary to the relations obtaining when the damping is proportional to the first power of the velocity.

In order to study the period of the oscillations return to equation (2). If V_0 is the velocity of the moving system when $\theta = 0$ then $V_0^2 = M/2N^2 + C_1$ and equation (2) may be written:

$$V^2 = \left(\frac{d\theta}{dt}\right)^2 = V_0^2 \mp 2V_0^2N\theta + 2C_1N^2\theta^2[1 \mp \tfrac{2}{3}N\theta + \tfrac{1}{3}N^2\theta^2 \mp \tfrac{2}{15}N^3\theta^3 + \cdots]. \tag{12}$$

If the product $N\theta$ is considerably less than one the expression within the brackets will not differ much from unity. We may therefore write

$$T - C = \int [V_0^2 \mp 2V_0^2N\theta + 2C_1N^2\theta^2]^{-1/2}d\theta = \sqrt{\frac{\epsilon^{(z_0-1)}}{Mz_0}} \sin^{-1}\left(\frac{-2C_1N^2\theta \pm NV_0^2}{\sqrt{N^2V_0^4 - 2C_1N^2V_0^2}}\right), \tag{13}$$

from which

$$\theta = -\frac{\sqrt{V_0^4 - 2C_1V_0^2}}{2C_1N} \sin\left[T\sqrt{\frac{Mz_0}{\epsilon^{(z_0-1)}}} - C'\right] \pm \frac{V_0^2}{2C_1N}. \tag{14}$$

If T_0 is the period of the oscillation then

$$T_0 = \frac{2\pi}{\sqrt{M}}\sqrt{\frac{\epsilon^{+2N/\theta_0/}}{(1 + 2N/\theta_0/)}}. \tag{51}$$

When N, the coefficient of damping, is zero $T_0 = 2\pi/\sqrt{M}$, which is the usual expression for the period of undamped harmonic vibrations. If $2N/\theta_0/ = 0.10$ the period is increased by 0.25 per cent. above that for undamped motion. This indicates that for moderate values of damping and displacement the period is lengthened slightly and the motion remains practically isochronous. If $2N\theta_0$ approaches a value of unity or greater, equation (15) is meaningless because the approximation employed is no longer valid. It may be shown experimentally, however, that for the larger values of $2N\theta_0$ the period is a little longer and the motion is still almost isochronous, just as in the case where the resistance varies as the first power of the velocity.

If values of θ are known at the successive turning points of the motion, by observation for example, an approximate value of N, the coefficient of resistance, may be found by a consideration of the energy relations during any one oscillation. At the initial position the velocity is zero and all of the energy is potential; this is true also at the next point of rest θ_1. The difference between the amounts of potential energy is equal to the dissipation of energy caused by the resistance, during the excursion from θ_0 to θ_1. Referring again to the torsion pendulum, if τ is the static moment of force per radian of twist in the suspending wire;

I_c is the moment of inertia, and N is the coefficient of resistance as before,

$$\frac{\tau}{2}[\theta_0^2 - \theta_1^2] = -NI_c\int_{\theta_0}^{\theta_1}\left(\frac{d\theta}{dt}\right)^2 d\theta. \qquad (16)$$

If $d\theta/dt$ can be expressed as an integrable function of θ, this equation will serve for the determination of N. Let the velocity be plotted in terms of displacement (Fig. 1) from equation (2), assuming for the moment any reasonable value of N. For moderate values of damping this curve during any one oscillation suggests a portion of an ellipse, with its center displaced from the origin of coördinates to the point corresponding to maximum velocity. That is, the motion is approximately simple harmonic about a center which is moved first to one side, then to the other side of the origin. Let θ' be the value of θ when the velocity is a maximum, and write $\alpha = \theta - \theta'$, then

$$\left(\frac{d\alpha}{dt}\right)^2 = \left(\frac{d\theta}{dt}\right)^2 = \frac{\tau}{I_c}[(\theta_0 - \theta')^2 - (\theta - \theta')^2] \qquad (17)$$

expresses the simple harmonic relation between velocity and displacement. Substituting in equation (16), integrating and solving for N, its approximate value is

$$N = 3\frac{[\theta_0^2 - \theta_1^2]}{[\theta_0 + /\theta_1/]^3}. \qquad (18)$$

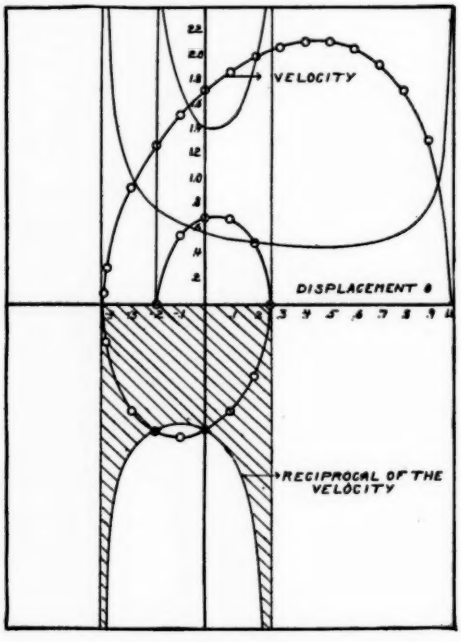

Fig. 1.

This approximate value may then be substituted in equation (10) and by successive trials a new value of N may be found which will correspond with the observed turning points, with any required degree of precision.

As a check upon the method of solution elaborated in the preceding pages, it may be noted that equation (2) can be integrated by graphical means. For example, let $N = 1.0$; $M = 10.0$; $\theta_0 = 1.0$ radian. If θ be taken as the independent variable and the reciprocal of the velocity be plotted against θ, the curve shown in Fig. 1 is obtained. Discon-

tinuity of resistance requires the use of the double sign in equation (2), and the constant of integration must be redetermined for each successive excursion. The area of any narrow strip extending from this curve to the axis of θ represents the amount by which T is increased, while the moving system passes through the corresponding angle. Using a planimeter, T may then be obtained in terms of θ by means of a step by step area summation. Plotting θ in terms of T, the curve shown in Fig. 2 is a graph of the motion demanded by the original differential equation.

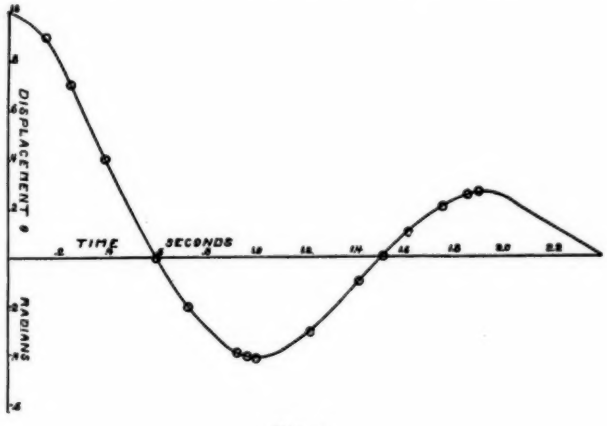

Fig. 2.

Plot of $\frac{d^2\theta}{dt^2} \mp 1.0 \left(\frac{d\theta}{dt}\right)^2 + 10.0\,\theta = 0$

Full Line by Fig. 1. Circles by equation (7).

To compare with the results of the graphical integration, the same values of N, M and θ_0 were substituted in equation (7). T was thus obtained for several values of θ. The results are shown as small circles placed upon the curve, Fig. 2. The agreement between graphical integration and the computations from equation (7) is apparent.

III. EXPERIMENTS.

Few attempts have been made to construct models for the study of oscillations damped by resistance varying with the square of the velocity. Durand[1] has suggested the use of small models of surge chambers and the extension of the results of observations, by the law of kinematic similitude, to surge towers of full size. No other reference has been found to any experimental means of reproducing and studying oscillations of this kind. It is obvious that any type of pendulum may be used, provided that the resistance is convertible into a function of the square of the velocity. It

[1] W. F. Durand, Trans. Amer. Soc. Mech. Eng., Vol. 34, p. 359, 1912.

will be advantageous to choose a model such that the coefficients of the resisting and the restoring forces can be varied at will, in which a minimum of inherent errors and unknown factors is introduced, and for which the required velocity is not so great as to render accurate observation difficult. There are doubtless many ways of obtaining an automatic adjustment of the resistance. Certain inherent difficulties appear to offset the advantages of automatic control; in the following pages a method depending essentially on electromagnetic induction is described, in which the necessary simplification is obtained by means of a manually operated device.

An annealed copper disk, 15 cm. in radius, is suspended from a rigid support by a phosphor-bronze torsion wire. The disk is accurately leveled and centered and oscillates between the jaws of a small soft iron electromagnet in such a manner that eddy currents are generated in the disk. The electromagnet is hung by a silk thread and hence is free to respond to the drag of the rotating disk caused by the Foucault currents. Attached to the lower jaw of the magnet is a small spiral spring which resists the tendency to turn, so that the actual displacement of the electromagnet from its position of equilibrium depends directly on the speed of rotation of the disk. The image of a brightly lighted, vertical slit is reflected from a mirror attached to the back of the magnet to a volt-potentiometer arranged in the form of an arc. The distance of the spot of light from the center of the arc thus gives a continuous measure of the velocity of the rotating disk.

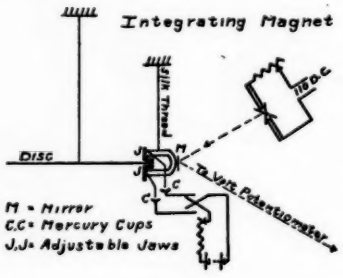

Fig. 3.

The volt-potentiometer consists of a meter stick bent into an arc of radius 55 cm. and effective length 60 cm. Every half centimeter there is a commutator segment consisting of a copper wire held firmly against the face of the stick. Each pair of segments equidistant from the center is connected through a fuse and switchboard to a supply of four volts from a large lead cell storage battery. Completing the circuit between the potentiometer center and the sliding contact are two pairs of specially designed damping coils, in the field of which the copper disk oscillates. Each of the coils has a radius of 6 cm., a wooden core of 2 cm. radius and is wound with 52 layers of number 20 enameled copper wire. The air gap in which the disk rotates is just large enough to permit perfect clearance. It is thus possible to obtain very heavy damping. The sliding

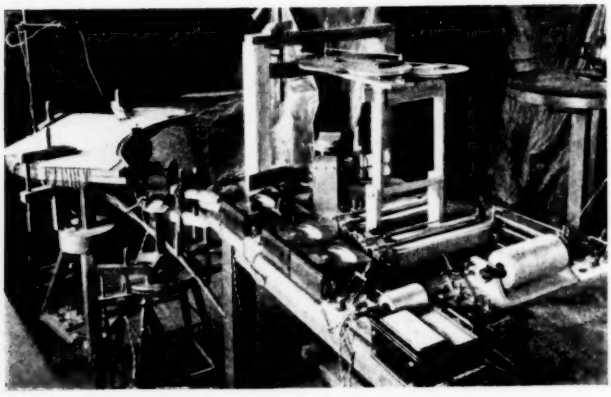

Fig. 5.

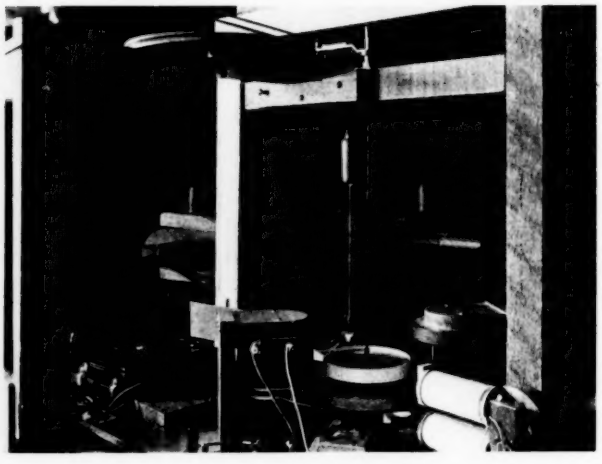

Fig. 6.

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contact on the volt-potentiometer is kept by hand under the spot of light reflected from the mirror on the integrating magnet. Hence at any instant the voltage across the damping coils is directly proportional to the velocity of the moving disk. Since there is no iron present and the speed of the disk is moderate, the current through the damping coils will vary sensibly as the voltage applied. Therefore the field set up by the coils varies directly as the velocity of the disk. Now the eddy currents generated in the rotating disk are directly proportional to the strength of the field, and the torque developed, which opposes the motion, is directly proportional to the product of the generated eddy currents and the existing field. Therefore the oscillations of the torsion pendulum are damped by a resistance varying as the square of the velocity. To regulate the value of the coefficient of damping it is only necessary to change the maximum voltage applied across the coils; or the deflection of the spot of light may be varied as desired, by changing the current actuating the electromagnet.

For the purposes of observation a circular millimeter scale 40 cm. in length is placed on the disk and turns with it. A fixed pointer leading out to the scale enables the successive turning points to be read with an accuracy of one part in four hundred, provided that the period of the swing is moderately large. If a continuous record of the displacement is desired a photographic record of the rotating scale may be taken. When the torsion wire is initially twisted, a device beneath the disk clamps the axle in such a manner that the disk may be released without jar. The torsion wire is joined to the disk by a small cap which is screwed on the axle, so that a new suspension may be substituted easily. The model may readily be adapted to show forced oscillations, motion damped by a combination of first power and second power resistance, rectilinear damping, and so on. (See Figs. 5–6.)

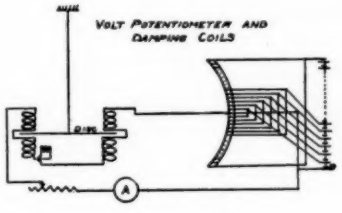

Fig. 4.

Considering the inherent errors of the apparatus: (1) There is always present a small amount of damping proportional to the first power of the speed. This is due to the drag of the integrating magnet and to the slight air friction on the upper and lower surfaces of the thin copper disk. (2) The current flowing in the coils and hence the field set up, is not exactly proportional to the voltage applied because the electromotive force is not constant but varying. In all of the measurements the resistance of this circuit in ohms was at least seventy times the inductance

of the damping coils, measured in henrys, and the period of oscillation of the disk was always greater than ten seconds. It may easily be shown by integration of the equation of electromotive forces that no appreciable error is introduced when the current is assumed proportional to the applied voltage. (3) An effect necessary to overcome was the influence of the varying field of the damping coils on the suspended magnet. To obviate this, a small coil was placed between the damping coils and the magnet and connected in series with the coils in such a way that its field almost entirely neutralized the troublesome stray induction. It was also found advantageous to maintain a weak general field about the magnet in order to reduce the importance of stray magnetic fields.

The copper disk weighing 755.5 grams was suspended by a No. 22 phosphor-bronze torsion wire, 35 cm. in length. From the change in the period due to the addition of a turned brass cylindrical disk weighing 976.5 gm. and also by direct computation from dimensions, the moment of inertia about the axis of support and the constant of the torsion wire were found; by means of these values the coefficient of the restoring torque, M, was found to equal 0.294 c.g.s. units. The natural, or undamped period, measured by chronograph and stop-watch, was 11.604 seconds. A current of 0.60 amperes was then sent through the electro-

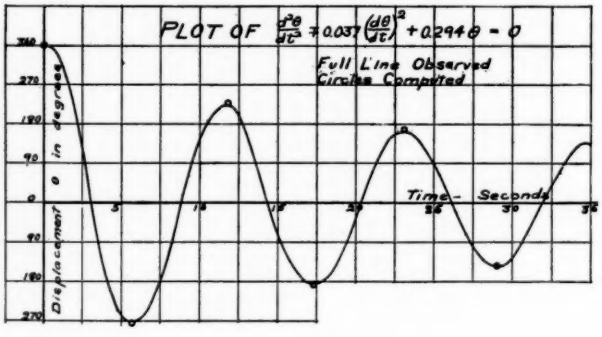

Fig. 7.

magnet circuit, a maximum voltage of 216 volts was applied across the potentiometer, the disk was displaced initially through 360 degrees, and turning points were observed. The motion is plotted in Fig. 7. The unknown coefficient of damping was found approximately, $N = 0.0370$. This value of N was used to determine from equation (10) the values of successive turning points, under the assumption of a resistance varying solely with the square of the velocity. The values are shown in Fig. 7 by circles. The effect of the small unavoidable damping, varying with the first power of the velocity, is apparent, the first, second, third and fourth

observed turning points lying a little inside of the computed values. It was found that the greatest variation from pure square damping between any two consecutive oscillations was 2.5 per cent. This is within the anticipated minimum of unavoidable error.

The next step was a more detailed comparison of the analytical solution, equation (7), with an experimental system. The restoring torque was maintained at its former value, but the coefficient of damping was increased by means of larger current in the damping coils. From several observations the first three turning points were found to be 360°, 197°, 149°. The new coefficient of damping was computed approximately from equation (18) and more precisely from equation (10). $N = 0.0960$. The constant of integration for equation (7) may be computed if we know the period of the oscillation. Experimentally the half-period, or the time for the first swing, was found to be 5.860 seconds. It may also be determined analytically from the relation

$$T\sqrt{M} = T_1\sqrt{M_1}(K), \qquad (19)$$

where T, M and T_1, M_1 are the half-periods and coefficients of the restoring torques, respectively, for two independent systems and (K) is the ratio of their correction factors (see equation (15)). Let us take T_1, M_1 for the case solved by graphical integration, Fig. 2; then $T = 5.840$ seconds, which is in close agreement with the experimental determination. All of the terms in equation (7) are now known. It may therefore be applied to the first oscillation in the manner already outlined. The graph of the motion is plotted in Fig. 8 and the values as computed by equation (7) are indicated by circles. It will be seen that the agreement is entirely satisfactory. For the second half-period, equation (7) is not applicable because the original expansion is not convergent. To determine the motion for the second oscillation analytically, it would be necessary to employ the expanded form resulting from the development of equation (8).

Figs. 7 and 8 exhibit the motion of the oscillating systems as practically isochronous. We have proved analytically that this is true for moderate damping. (See equation (15).) It may also be shown experimentally. A smoked drum chronograph 50.5 cm. in circumference was driven by a small motor connected through a friction drive and reduction gears. Two needle pointers mounted on a traveling screw traced continuous paths on the drum. One pointer was actuated by a contact on the pendulum of a laboratory clock so that it indicated seconds. The other pointer, by means of a tapping key, was made to record the successive instants at which the torsion pendulum passed through its position of

equilibrium. For the motion of the oscillating system plotted in Fig. 7 five independent records of the times for successive swings were taken and the first nine average values were found to be 5.81, 5.85, 5.77, 5.87, 5.77, 5.83, 5.78, 5.81, 5.82 seconds. The average half-period was a little more than 5.81 seconds and the greatest deviation from the average was

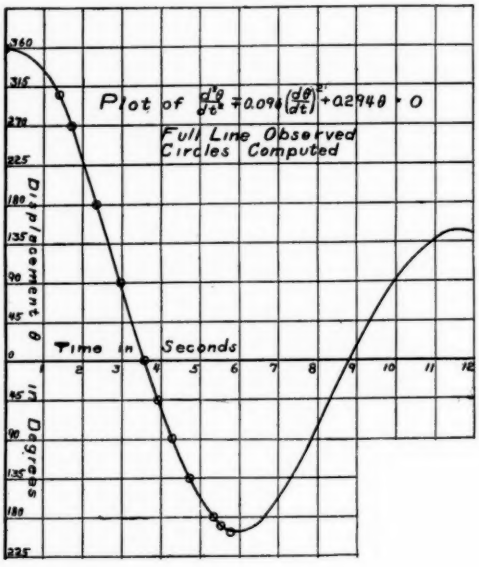

Fig. 8.

0.06 second, or approximately one per cent. This is well within the expected accuracy, since it is probable that for any single observation an error of one tenth of a second would easily enter in tapping the key a little too soon or too late. We are therefore furnished with experimental evidence that for moderate and even heavy damping the oscillations are practically isochronous.

IV. Use of the Experimental Model in the Study of Other Forms of Damped Oscillations.

It has been mentioned that the model described in Part III. is capable of extension to other problems in damped harmonic motion. Of these problems, three have been given some consideration, experimentally and analytically. These are: (1) free oscillations subject to both first and second power damping, the first power predominating; (2) forced, continuous vibrations; (3) rectilinear damping. A detailed discussion of each case is beyond the scope of this paper. We shall merely point out the lines along which the investigation has proceeded.

1. In order to produce a resisting torque due to both first and second power damping it is only necessary to add to the existing arrangement a constant damping field. By means of a small coil with an iron core (demagnetized before each setting), through the field of which the disk rotates, a wide range of damping is readily obtained. (See Fig. 6.) One feature of the greatest advantage lies in the ability to study each of the two components of the damping singly as well as combined. We may therefore make an independent determination of each coefficient of damping apart from the more complicated motion due to their joint action. Analytically the oscillations may be treated by the double approximation method of Routh,[1] provided that the first power damping predominates. The following conclusions have been established experimentally for systems having an initial displacement of 2π radians: (*a*) the oscillations are isochronous; (*b*) the period is increased somewhat by an increase in either or both components of the damping; (*c*) the ratio of arcs is at first greater and then less than the average value; (*d*) successive differences for the combined damping are at first greater and then less than for the first power damping alone; (*e*) the influence of the second power damping rapidly diminishes and the decrement approaches its value for pure first power resistance. This is to be expected since a decrease in the velocity to one half its original value reduces the second power damping to one fourth its initial effectiveness.

2. Forced oscillations may be produced by twisting the torsion wire periodically. To accomplish this, an arm is rigidly attached to the torsion wire head and is driven back and forth harmonically by means of a connecting rod, slotted cross head and reduction gears. (See Fig. 5.) If higher harmonics are desired in the forcing term, a combination of gears such as are used in a curve-tracer may be employed to turn the torsion wire. Following Routh's double approximation method a solution may be developed for systems in which the amount of damping is small.

3. The influence of a constant damping factor, independent of the speed, on the motion of an oscillating system becomes of importance in several interesting connections. Thus from the equations derived by Durand[2] for the surge-chamber problem in hydraulics, if the effect of governor control is neglected and the motion of the water is expressed solely in terms of displacement in the surge tower, there results an equation of the type

[1] E. J. Routh, Adanced Rigid Dynamics, p. 251, 1905. The solution given by Routh (Art. 364) is limited to displacements so small that their squares and higher powers may be neglected. It is possible, however, following Routh's general method to develop a solution not limited by the magnitude of the displacement.

[1] W. F. Durand, *op. cit.*, p. 321, 1912.

$$\frac{d^2\theta}{dt^2} \pm A\left(\frac{d\theta}{dt}\right)^2 + B\left(\frac{d\theta}{dt}\right) + C\theta + D = 0. \tag{20}$$

Here there are present three types of damping: that varying with the first power of the speed; that varying with the second power, and a constant resistance independent of the speed. The model which has been developed may be adapted to exhibit just such a type of resisted motion.

In connection with electrical instruments subject to pivot friction and in certain oscillating systems, Blondel and Carbenay[1] have shown that the oscillations are represented by an equation of the type

$$\frac{d^2\theta}{dt^2} + B\left(\frac{d\theta}{dt}\right) + C\theta + D = 0 \quad (\text{or} = A \sin(\omega t)). \tag{21}$$

An electrical analogy is found in an oscillating circuit of radio frequency in which spark resistance predominates.[2] An experimental study of motion corresponding to the type equation (21) may readily be made. It is beyond the limits of this paper, however, to enter into a discussion of these allied problems in resisted oscillations. Enough has been suggested, perhaps, to indicate the flexibility of the model developed and the wide range of problems for which there is now a means of experimental study.

SUMMARY.

1. A complete solution has been developed for the equation

$$\frac{d^2\theta}{dt^2} \pm N\left(\frac{d\theta}{dt}\right)^2 + M\theta = 0,$$

subject only to one limitation, namely:

$$\frac{(1 \pm 2N\theta_0)\epsilon^{1\pm 2N\theta}}{\epsilon^{1\pm 2N\theta_0}(1 \pm 2N\theta)} \neq 1.$$

2. The solution has been verified by comparison with the results of graphical integration and by experiment.

3. The oscillations have been shown analytically and experimentally to be practically isochronous.

4. A solution has been developed by which the numerical values of the successive turning points may be computed.

5. A model has been constructed suitable for a wide range of systems by means of which it is possible to study oscillations damped by resistance proportional to the square of the velocity.

[1] A. Blondel and F. Carbenay, La Lumière Élec., Nov. 27, Dec. 4, 11, 1915, and July 29, 1916.

[2] A. W. Stone, Inst. Radio. Eng., Proc. 2, pp. 307–427, Dec., 1914.

6. A method is given for the determination of the coefficient of damping in terms of the values of the successive turning points.

7. The model developed may be extended to exhibit: (*a*) forced oscillations; (*b*) systems resisted by both first and second power damping; (*c*) systems resisted by a constant factor, alone or in combination with other forms of damping.

8. The prevalence of damping proportional to the square of the speed in problems of resisted motion has been demonstrated by a survey of the literature. A bibliography is given for the more important engineering cases in which this type of oscillation occurs.

In conclusion, the author takes pleasure in expressing his thanks to Prof. W. J. Raymond, Prof. B. M. Woods, Prof. F. E. Pernot and others, whose valuable suggestions and friendly criticisms have been most helpful.

PHYSICAL LABORATORY, UNIVERSITY OF CALIFORNIA,
May, 1917.

THEORY OF CRYSTAL STRUCTURE, WITH APPLICATION TO TWENTY CRYSTALS BELONGING TO THE CUBIC OR ISOMETRIC SYSTEM.

BY ALBERT C. CREHORE.

IN a former communication[1] an expression for the mechanical force between any two atoms in their most general positions was derived from the early form of electromagnetic equations proposed by Thomson.[2] The assumption was made that these equations apply to the individual electrons in the atoms, each revolving in circular orbits around a common center determined by the positive charge, and that the atoms are neutral, the total positive charge being numerically equal to the sum of the negative charges. The total force between the atoms is obtained by the summation of the forces between their various parts. To obtain the forces between the two positive charges, and between the positive charge of the one and an electron in the other, presents little difficulty because the ordinary electrostatic forces apply in these cases. The problem then resolves itself into that of finding the average force between two electrons supposed to be revolving in circular orbits with uniform velocity, the circles being in their most general positions in space. The result for two atoms is given by equations (23)–(25), page 755 of the paper referred to.

More recently[2] the same problem has been solved for two atoms using the Lorentz form of the electromagnetic equations, involving the conception of retarded potentials which does not form a part of the older Thomson equations. The expression for the average force is finally developed in both cases in the form of infinite series of the inverse powers of r, the distance between the centers of the two atoms. In the Lorentz form the series begins with the inverse first power of r and all inverse powers of r are present. When, however, the force is resolved along the line joining the centers of the two atoms this series begins with the inverse square term. If the distance between the atoms is large, the first term is the only one which is effective, and we have in this result the suggestion that this force may be identical with that of gravitation. A critical

[1] Phil. Mag., June, 1915, p. 750.

[2] J. J. Thomson, Phil. Mag., April, 1881, p. 229.

[3] PHYS. REV., June, 1917.

examination has shown that this force resembles that of gravitation in many ways, in being always an attraction and never a repulsion, and in being independent of the orientation of the axes of rotation of the atoms, so that two crystals have the same pull no matter how they are oriented. But, in the matter of the magnitude of the force, the theory demands a force more than 10^{30} times greater than the force of gravitation really is. This result compels the belief that these Lorentz equations in their present form without modification do not apply to the electrons in the atoms of matter.

However, it is found that, when the expression for the inverse square terms thus derived is multiplied by a factor proportional to the kinetic energy of the electron itself, the correct value of the gravitational pull is obtained. This has given some reason to hope that a modification in the present form of the electromagnetic theory will be found that will make it strictly applicable to the electrons in the atoms when in their steady state not radiating energy. At any rate, I have taken the liberty of introducing the factor demanded by the inverse square terms into the Lorentz forms, thus making a modified form of the present statement of these equations, and find that in so doing the average force between two atoms, at the distances apart concerned in crystals, agrees very closely with the result derived from the older Thomson form of the electromagnetic equations. The first, second, and third terms of the series become ineffective at this range, and, when account is taken of the space-lattice formation of cubic crystals, the series begins with the inverse fourth power, the even powers only following this.

This is precisely the form of equation obtained from the Thomson theory, above referred to, the only difference between the two forms, after introducing the modification, being a factor of 2 in some of the terms in r^{-4}. This factor of 2, however, makes some difference in applying these results to crystals, and, of the two forms, the Thomson equations give consistent results, showing stable equilibrium when we consider the odd planes, as in rock salt, or the even planes as in copper; whereas, the other form gives equilibrium for the odd planes only, but not for the even. The consideration of crystals affords a test between the two forms, and indicates that the Thomson form is to be preferred for these small distances because the results using the odd planes, as in NaCl, KCl, KBr, etc., fit very closely those using the even planes, as in Cu, Fe, Ag, Pd, etc., whereas the other form does not.

The above remarks give some justification for the use of the following equation for the force between two atoms at close range, based upon the Thomson theory. Since the z or k component of the force, that acting

along the direction of the axis of rotation of the atom, is the only one that we shall require, this is repeated here. The reason that the i and j components are not required is that cubic crystals are so arranged that these components each cancel out in summing the effects of surrounding atoms upon a single selected atom. That is to say, the total force due to all other atoms added together upon the one has the direction of its axis of rotation.

$$\begin{aligned} F_z = e^2\{&\textstyle\sum_P (a\beta) \sum_{P'} (a\beta)[+1.5n\cos\alpha + .75l\sin\alpha - 3.75m^2n\cos\alpha - 3.75ln^2\sin\alpha \\ &-3.75l^2n\cos\alpha]r^{-4} \\ &-\textstyle\sum_P a^2 \sum_{P'} a^2[+5.625n + 3.75n\sin^2\alpha + 7.5l\sin\alpha\cos\alpha + 1.875n\cos^2\alpha \\ &-13.125(+l^2n + 4m^2n + n^3\sin^2\alpha + 3l^2n\cos^2\alpha \\ &+4ln^2\sin\alpha\cos\alpha + l^2n\sin^2\alpha + l^3\sin\alpha\cos\alpha + m^2n\sin^2\alpha \\ &+lm^2\sin\alpha\cos\alpha) \qquad (1) \\ &+59.0625(+l^2n^3\sin^2\alpha + l^2m^2n + l^4n\cos^2\alpha + m^2n^3\sin^2\alpha + m^4n \\ &+l^2m^2n\cos^2\alpha + 2l^3n^2\sin\alpha\cos\alpha + 2lm^2n^2\sin\alpha\cos\alpha)]r^{-6}\}k. \end{aligned}$$

In this equation e is the charge of the electron, a the radius of its orbit, and β the ratio of its velocity to that of light. P is the number of electrons in the first, and P' in the second atom. The summations indicated in the coefficients are to be extended to each electron in each atom respectively. l, m, and n are the direction cosines of the center of the second atom with respect to the center of the first, referred to rectangular axes, xi, yj, and zk, having the origin at the center of the first atom. The positive direction of the zk axis is that of the axis of rotation of the first atom, so that the rotation is clockwise viewed from the positive end. The positive direction of the yj axis is then defined by the vector $k \times k'$, k' being the unit vector in the direction of the axis of rotation of the second atom. This vector takes the direction of the intersection of the equatorial planes of the two atoms, being perpendicular to both k and k', and the positive direction is such that rotation from k to k' appears counterclockwise viewed from the positive end. The quantities in the brackets are functions of the position of the second atom and the direction of its axis with respect to the first atom. These expressions become numerics as soon as the position of the second atom is known, that is, when the form of the space-lattice of a crystal is specified. The equation may be written[1]

[1] The letter l has inadvertently been employed in two senses here, first as a direction cosine in the functions, f_4 and f_6, and then as the cube edge in l^{-4} and l^{-6}, but no confusion will arise from this.

$$F_x = e^2\{f_4(l, m, n, \alpha) \sum_P (a\beta) \sum_{P'} (a\beta) l^{-4} + f_6(l, m, n, \alpha) \sum_P a^2 \sum_{P'} a^2 l^{-6} \cdots\} k. \quad (2)$$

The two quantities, $\Sigma_P(a\beta)$ and $\Sigma_P a^2$, are characteristic properties of the atoms, and it is the purpose of this investigation to learn something about them, as far as anything can be ascertained from a study of crystals. In the case of the diamond[1] an example has been given of the arrangement of the planes and directions of the axes of rotation of each atom, to which reference is made, in which it is found that the equation for the total force on one atom due to the others may be written

$$F_x = e^2\{-15.7225 \sum_P (a\beta) \sum_{P'} (a\beta) l^{-4} + 252.83 \sum_P a^2 \sum_{P'} a^2 l^{-6} \cdots\} k, \quad (3)$$

where l is the edge of the elementary tetrahedron. Since this is $\sqrt{2}$ times the cube edge, the above becomes

$$F_x = e^2\{-3.9306 \sum_P (a\beta) \sum_{P'} (a\beta) l^{-4} + 31.604 \sum_P a^2 \sum_{P'} a^2 l^{-6} \cdots\} k, \quad (4)$$

where l is now the cube edge. When this force is equated to zero for the equilibrium condition, we obtain, putting $d = 31.604/3.9306 = 8.04$,

$$\frac{\sum_P (a\beta) \sum_{P'} (a\beta)}{\sum_P a^2 \sum_{P'} a^2} = \frac{d}{l^2} = \frac{8.04}{l^2}. \quad (5)$$

A similar process has been carried out for the 124 atoms surrounding the central atom in a *simple cubic lattice* of edge $4l$, (see appendix) giving, for the odd planes on one half of the cube only,

$$F_x = e^2\{0.6013 \sum_P (a\beta) \sum_{P'} (a\beta) l^{-4} - 4.6455 \sum_P a^2 \sum_{P'} a^2 l^{-6} \cdots\} k, \quad (6)$$

and, for the even planes on one side only,

$$F_x = e^2\{-0.49517 \sum_P (a\beta) \sum_{P'} (a\beta) l^{-4} + 0.94059 \sum_P a^2 \sum_{P'} a^2 l^{-6} \cdots\} k. \quad (7)$$

Equating these to zero gives for the odd planes

$$\frac{\sum_P (a\beta) \sum_{P'} (a\beta)}{\sum_P a^2 \sum_{P'} a^2} = \frac{v}{l^2} = \frac{7.73}{l^2}, \quad (8)$$

and, for the even planes,

$$\frac{\sum_P (a\beta) \sum_{P'} (a\beta)}{\sum_P a^2 \sum_{P'} a^2} = \frac{u}{l^2} = \frac{1.90}{l^2}. \quad (9)$$

Experimental evidence from measurements with the X-ray spectrometer gives the cube edge, l, and the form of lattice, but nothing else in these equations. From such data we obtain merely the ratios in the left

[1] Phil. Mag., Aug., 1915, p. 257.

hand members of (5), (8) and (9), the right members becoming simple numbers when the values of l are substituted.

It is at this point where some kind of hypothesis concerning the quantities a and β, as relating to the atoms, is required. Heretofore, in the papers referred to, the equal moment of momentum hypothesis was introduced for lack of something better, though there seemed to be no very urgent reason why this should be true. The quantity $a\beta$ is proportional to this angular moment of momentum, and, if this has the same value for each electron in the atoms, the quantity in the numerator of the left member of these equations is much simplified, becoming PP' times a constant, these being the number of electrons respectively in the atoms. If we should make this assumption, the values of Σa^2 for the different atoms in the crystals considered might be found in terms of this constant.

Since, however, we have been able to calculate the speed of rings of electrons, that of four being $\beta = .00846$, and of eight $\beta = .012$, it is evident that the natural tendency of the outer rings is to have a greater actual velocity than the inner rings, if the outer ring has a greater number of electrons. The equal angular moment of momentum hypothesis, however, demands a greater velocity for the smaller ring, the velocity being twice as great at half the radius, and the differential angular velocity between different rings is very pronounced. On the other hand, the calculation of the speed of rings seems to make the angular velocities more nearly equal for different radii. If, for example, the radii were in the ratio of the above speeds, that of the ring of eight being 12 and of the ring of four 8.46, the angular velocities of the two rings would be the same.

It seems neither safe to assume an equal angular moment of momentum nor an equal angular velocity for each electron in the light of present knowledge. There is another investigation, however, which has a direct bearing upon this matter. The tentative formula for the weight of an atom due to the earth's attraction, to which reference has been made, is

$$F = \frac{1}{8}\frac{m}{K} m_0 e_1 e_2 \Sigma_P \beta^2 \Sigma_E \beta^2 r_E^{-2} = k \Sigma_P \beta^2, \tag{10}$$

where

$$k = \frac{1}{8}\frac{m}{K} m_0 e^2 r_E^{-2} \Sigma_E \beta^2, \tag{11}$$

the first summation being extended over a single atom, and the second over all the atoms composing the earth, which is, of course, a constant quantity if we are merely comparing the weights of two atoms. r_E is the radius of the earth. This result indicates that the weight of an atom is

strictly proportional to the sum of the squares of the linear velocities of the electrons within the atom. Since the weights of atoms are constant in the same locality, we may better assume that $\Sigma_P \beta^2$ is constant for a given atom. This quantity, however, does not occur, directly anyway, in the equations (5), (8) and (9), by which we have to investigate crystals.

The solution for the speed of rings of electrons also shows that the linear velocity is independent of the radius of the ring, and, hence, coupling this with the suggestion as to the cause of the weight, we see that it is quite possible that the radii of the orbits of the electrons in an atom may change without affecting the speeds, or consequently, their weights. But, as the radius increases, the angular velocity decreases proportionally in order to maintain the same actual velocity. We may write the three quantities for the atoms, with which we are concerned as follows,

$$\sum_P a^2 = a_1^2 + a_2^2 + a_3^2 + \cdots a_P^2, \tag{12}$$

$$\sum_P (a\beta) = \frac{I}{c}(a_1^2\omega_1 + a_2^2\omega_2 + a_3^2\omega_3 + \cdots a_P^2\omega_P), \tag{13}$$

$$\sum_P \beta^2 = \frac{I}{c^2}(a_1^2\omega_1^2 + a_2^2\omega_2^2 + a_3^2\omega_3^2 + \cdots a_P^2\omega_P^2). \tag{14}$$

For a single ring atom the values of a and ω are the same for each electron, and, for a ring of P electrons, we have

$$\sum_P a^2 = Pa^2, \tag{15}$$

$$\sum_P (a\beta) = \frac{P}{c} a^2\omega, \tag{16}$$

$$\sum_P \beta^2 = \frac{P}{c^2} a^2\omega^2. \tag{17}$$

From these we have, for a single ring atom,

$$\frac{\Sigma(a\beta)}{\Sigma a^2} = \frac{\Sigma\beta^2}{\Sigma(a\beta)} = \frac{\omega}{c}, \quad \text{or} \quad [\Sigma(a\beta)]^2 = \Sigma\beta^2 \Sigma a^2. \tag{18}$$

For a multiple ring atom we may use a mean square radius, mean velocity, and mean square velocity, giving instead of (12)–(14)

$$\sum_P a^2 = Pa_0^2, \tag{19}$$

$$\sum_P (a\beta) = \frac{P}{c} \omega_1 a_0^2, \tag{20}$$

$$\sum_P \beta^2 = \frac{P}{c^2} \omega_2^2 a_0^2. \tag{21}$$

The subscripts are used in connection with the angular velocities because the two mean velocities obtained in this way are not exactly the same. To show by how much they differ from each other in a special case, an example is given below. We obtain from (19)–(21)

$$\frac{\sum_P(a\beta)}{\sum_P a^2} = \frac{\omega_1}{c} \tag{22}$$

$$\frac{\sum_P \beta^2}{\sum_P(a\beta)} = \frac{\omega_2^2}{c\omega_1}. \tag{23}$$

In a two-ring atom, let the radius of the outside ring be a, speed such that $\beta = .012$, and number of electrons eight. For the inside ring let $a_i = .402\,a$, $\beta_i = .00846$, and the number of electrons four. Then, for the atom

$$\sum_P a^2 = 8a^2 + 4(.402a)^2 = 8.6464a^2 = Pa_0^2 = 12a_0^2, \tag{24}$$

$$\sum_P(a\beta) = 8a \times .012 + 4 \times .402a \times .00846 = .1096a$$

$$= \frac{P}{c}\omega_1 a_0^2 = \frac{12}{c}\omega_1 a_0^2, \tag{25}$$

$$\sum_P \beta^2 = 8 \times .012^2 + 4 \times .00846^2 = .001438 = \frac{P}{c^2}\omega_2^2 a_0^2 = \frac{12}{c^2}\omega_2^2 a_0^2, \tag{26}$$

$$\frac{\sum_P(a\beta)}{\sum_P a^2} = \frac{.01268}{a} = \frac{\omega_1}{c} \tag{27}$$

$$\frac{\sum_P \beta^2}{\sum_P(a\beta)} = \frac{.01312}{a} = \frac{\omega_2^2}{c\omega_1}, \tag{28}$$

whence

$$\left(\frac{\omega_2}{\omega_1}\right)^2 = \frac{.01312}{.01268} = 1.034, \quad \text{and} \quad \frac{\omega_2}{\omega_1} = 1.017. \tag{29}$$

According to this example we do not make much error in assuming that equation (18), which is strictly true for the single ring atom, is also approximately true for more complicated forms. Making this approximation, (5) becomes

$$\sum_P a^2 \sum_{P'} a^2 = \frac{l^4}{d^2}\sum_P \beta^2 \sum_{P'} \beta^2; \tag{30}$$

with similar expressions for (8) and (9), the differences being in the values of the constants.

But, by (10), we may consider that $\Sigma_P \beta^2$ is constant for a given atom, and thus may find its value from the atomic weight. If W is the atomic

weight in dynes, and A the atomic weight referred to oxygen as 16, then W is equal to A times the weight of the hydrogen atom divided by 1.008. Taking the mass of the hydrogen atom as 1.64×10^{-24} grams, and its weight $1.64 \times 981 \times 10^{-24}$ dynes, the weight of any atom is

$$W = 15.96 \times 10^{-22} A_P = k \sum_P \beta^2, \quad \text{by (10).} \tag{31}$$

Hence

$$\sum_P \beta^2 = 15.96 \times 10^{-22} A_P / k = k_1 A_P, \tag{32}$$

where

$$k_1 = 15.96 \times 10^{-22} / k. \tag{33}$$

Putting this in (30) gives as the equilibrium condition for the diamond form of lattice,

$$\sum_P a^2 \sum_P a^2 = \frac{k_1^2}{d^2} A_P A_{P'} l^4. \tag{34}$$

For a crystal like rock salt we obtain from (8) a similar form to this, with the constant[1] d equal to 7.73 instead of 8.04, being obtained from the odd planes of the simple cubic lattice, and for copper from (9) a similar form with the constant 1.90, obtained from the even planes of the simple cubic lattice, in this case the even planes being the only ones present.

These formulæ have been applied to twenty different crystals belonging to the cubic or isometric system, some of which are known to have been examined by the spectrometer and others not. In certain cases the formulæ give Σa^2 directly, when there is but one kind of atom in the crystal, as diamond, copper, silver, iron, etc., but in most cases they give products $\Sigma_P a^2 \Sigma_{P'} a^2$ for the two kinds of atoms that enter the crystal. The separate values in this case for each kind of atom may only be obtained when one of them is known from some other crystal.

The remarkable result is obtained that Σa^2 shows a gradual progression from element to element, the irregularities being of about the same order as the irregularities in atomic weights. The curves obtained from these twenty crystals, containing as many separate kinds of atoms altogether, are shown in Figs. 1 and 2. The best values of Σa^2 and $\Sigma(a\beta)$ to agree with the different crystals are plotted for each of the twenty elements as separate points.

It is found, however, that, in order to make the points fall near the curves, the calculation must be made for some of the crystals as though there were double instead of single atoms at each point of the space lattice. The points either fall near the curve for the correct form of lattice and proper number of atoms, or very far from it for a wrong

[1] See equation (5) above.

combination. The compounds of sulphur may serve as an illustration. The crystals, zincblende (ZnS, diamond lattice) and galena (PbS, rock salt lattice), have been studied by the spectrometer, and the measured spacings of the planes agree with those calculated from their densities, on the assumption that there is but a single atom of zinc and a single atom of sulphur at the points of the lattice. The points, as calculated by the above formulæ with this spacing, do not fall anywhere near the curve, but, if we had calculated the lattice on the assumption that the atoms of each were double at the various points, we should have obtained an edge for the elementary cube $2^{1/3}$ greater than before, and the product $\Sigma_p a^2 \Sigma_{p'} a^2$ would have been $2^{4/3}$ greater, depending upon the fourth power of l. The points for zinc and sulphur thus obtained fall near these curves.

TABLE I.

List of Crystals and Elements from Which the Curve in Fig. 1 is Obtained.

No.	Crystal.	Lattice.	Elements.
1	NaCl	Rock salt	C
2	KCl	"	O
3	KBr	"	F
4	KI	"	Na
5	AgCl	"	S
6	AgBr	"	Cl
7	PbS	"	K
8	PbTe	"	Ca
9	MnS	"	Mn
10	CuO	"	Fe
11	Diamond	Diamond	Cu
12	ZnS	"	Zn
13	CaF_2	Fluorspar	Br
14	FeS_2	Iron pyrites	Pd
15	Cu	Copper	Ag
16	Fe	"	Te
17	Pd	"	I
18	Ag	"	Pt
19	Pt	"	Au
20	Au	"	Pb

In the case of galena we have to assume four atoms of lead and four of sulphur instead of one at the points of the lattice, making l greater by $2^{2/3}$, and l^4 by $2^{8/3}$, than it really is to make the points fall near the curves. Since the spectrometer has definitely settled the question of the length of the elementary cube of the space lattice, we can not suppose that

there are double atoms in zincblende and quadruple atoms in galena at the points of the lattice, and, according to the hypothesis that $\Sigma\beta^2$ is proportional to the weight, we are led to believe that Σa^2 is not always the same in some kinds of atoms at least.

If we consider that manganblende, MnS, is a simple cubic lattice like rock salt, the values of Σa^2 fall near the curve by assuming double atoms.

Another crystal containing sulphur is iron pyrites, which has been described by W. H. and W. L. Bragg in " X-rays and Crystal Structure " in much detail. If we apply the same equilibrium formula to this as applies to diamond, zincblende and fluorspar, we obtain points close to the curve by assuming double atoms. How it is possible that the same equilibrium condition may be applied to such different lattices is shown in the appendix hereto.

The point we are now making is that these four crystals fall into line if we admit that there are two different kinds of sulphur atoms, the same kind of sulphur in ZnS, MnS, and FeS_2, and a different kind in PbS, their weights being the same in each case, but Σa^2, $\Sigma(a\beta)$ and ω_1 differing for the two kinds. To fall upon the curve in Fig. 1, the sulphur atom should have approximately

$$\sum_P a^2 = 300 \times 10^{-16} \frac{k_1}{v}.$$

In ZnS, MnS, and FeS_2 the value required is $(\frac{1}{2})^{4/3} = .397$ of this, and in PbS $(\frac{1}{2})^{8/3} = .1575$ of it. The value corresponding to the curve does not occur in these crystals, but it seems likely that it does occur sometimes, perhaps in other crystals.

A similar statement may be made for the atoms of oxygen, chlorine, and bromine. By admitting two possible forms for these three atoms, having the same atomic weight in each case, all of the twenty crystals considered are brought into line. Chlorine and bromine in the halogens, NaCl, KCl, KBr have values of Σa^2 corresponding to the curve, but, in AgCl and AgBr, the Cl and Br have values $(\frac{1}{2})^{4/3} = .397$ of that in KCl and KBr. In the mineral melaconite, CuO, the oxygen has a value of $\Sigma a^2\ (\frac{1}{2})^{4/3}$ of that given by the curve. This is the only crystal considered containing oxygen. It seems likely that a value of oxygen will be obtained from other crystals which agrees with the curve. The only crystal containing fluorine, CaF_2, gives a value close to the curve. We seem justified in expecting to find in other crystals a value equal to $(\frac{1}{2})^{4/3}$ of this for *F*.

In Fig. 2 the atomic weights of the elements are plotted with reference to the atomic numbers, and a mean curve drawn through the points. By equation (32) we may obtain from this the values of $\Sigma\beta^2$ when the

abscissæ of this curve are multiplied by the constant k_1. The approximate value of $\Sigma(a\beta)$ may then be derived by multiplying together the corresponding abscissæ of Σa^2 in Fig. 1 and $\Sigma\beta^2$, and taking the square root of the product, according to (18). The curve of $\Sigma(a\beta)$, thus obtained, is shown in II., Fig. 2. And, according to (22), we may obtain the mean angular velocity of revolution of all the electrons in the atoms by dividing $\Sigma(a\beta)$ by Σa^2, which is shown in Curve III., Fig. 2.

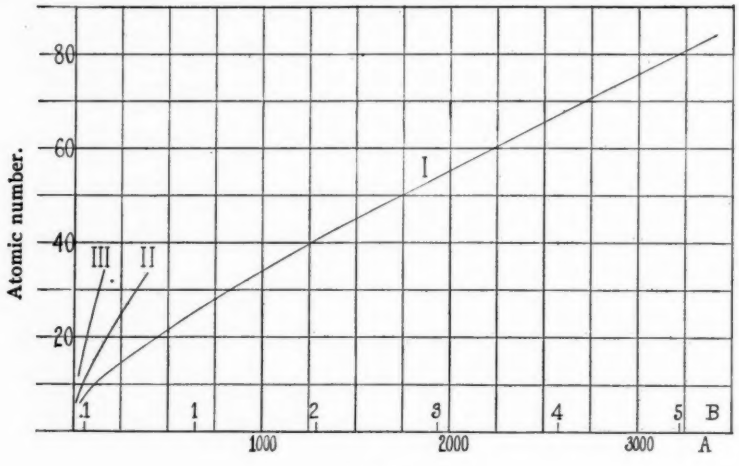

Fig. 1.

Curves I., II. and III. $\frac{v}{k_1}\sum_P a^2 \times 10^{16}$. Scale *A*.

Curves I., II. and III. $\sum_P a^2 \times 10^{18}$ sq. cm. Absolute scale *B*.

The character of the curve of Σa^2, Fig. 1, supports the theory that the electrons are distributed in rings resembling those originally calculated by Thomson, and that the volume of the sphere enclosing the rings increases by uniform steps as electrons are added. The volume of a sphere enclosing the orbits of the electrons, on the assumption that they are arranged in a plane, may be taken roughly proportional to the cube of the mean radius. The mean square radius is proportional to $\Sigma a^2/N$, where N is the atomic number, and the volume, therefore, proportional to $(\Sigma a^2/N)^{3/2}$. If the volume is also proportional to the number of electrons, and this again to the atomic number, we derive the equation

$$\left(\frac{\Sigma a^2}{N}\right)^{3/2} = N \text{ times a constant,}$$

Hence

$$\Sigma a^2 = bN^{5/3}, \text{ where } b \text{ is a constant.} \qquad (35)$$

The values of Σa^2 read from the curve, and $N^{5/3}$ calculated from the corresponding atomic numbers, are as follows:

TABLE II.

N.	$N^{\frac{5}{3}}$.	Σa^2.	$\frac{\Sigma a^2}{N^{\frac{5}{3}}}$.
10.....	46.3	110	2.38
20.....	147.3	442	3.00
30.....	289.4	830	2.87
40.....	469.	1,263	2.7
50.....	679.	1,745	2.57
60.....	920.	2,235	2.43
70.....	1,189.	2,713	2.28
80.....	1,485.	3,213	2.16
90.....	1,806.	3,712	2.06

The constancy of this ratio in the above table is as nearly perfect as we should expect, were it exactly true that the volume of a sphere enclosing the outside rings increases by equal steps for the addition of each electron, because of the approximation we are forced to use in deriving the result in (35).

The curve for $\Sigma(a\beta)$ in Fig. 2 is very nearly a straight line for the atomic numbers above 40, Zirconium; but the line does not pass through the origin. If we dvide $\Sigma(a\beta)$ by N, to obtain the average moment of momentum per electron, these exhibit a gradual increase with increasing atomic numbers. The average for the heavier elements is sufficiently constant to have suggested the idea that the angular moment of momentum for each electron is constant,[1] but, in the lighter elements, these values vary considerably from those in the heavy elements.

The curve for the mean angular velocity of each atom, III., Fig. 2, shows a decrease in the frequency for an increase in the atomic number. The frequency becomes very large for the lightest elements. For carbon this frequency, as we shall see by the two examples, is about $.78 \times 10^{18}$. The average frequencies for the other elements are obtained from the ratio of the abscissæ of Curve I. to those of Curve II., Fig. 2, and, since Curve II. approaches zero much more rapidly than Curve I., the ratio and the frequency become rapidly larger for decreasing atomic numbers. The fundamental value for hydrogen has been found elsewhere[2] to be of the order of 10^{20}, considerably greater than that for carbon.

If one identifies the frequencies of revolution of the electrons in their orbits with optical frequencies according to Bohr's theory, the radii of the orbits, being inversely as the frequencies, come out much greater than the orbits indicated by the above *average* values of the frequencies.

[1] Moseley, Nature, Jan. 15, 1914, and F. A. Lindemann, Nature, Jan. 1, Feb. 5, 1914.

[2] Unpublished.

It is possible, of course, that a small number of electrons circulate in large orbits with smaller frequencies, and that the rest have very much smaller orbits and higher frequencies, so far as we can tell from these *average* values. If this is true, then the electromagnetic forces, as developed in infinite series cannot be applied to these outside electrons, because the force-series becomes non-convergent when the distance between the centers is comparable with the diameter.

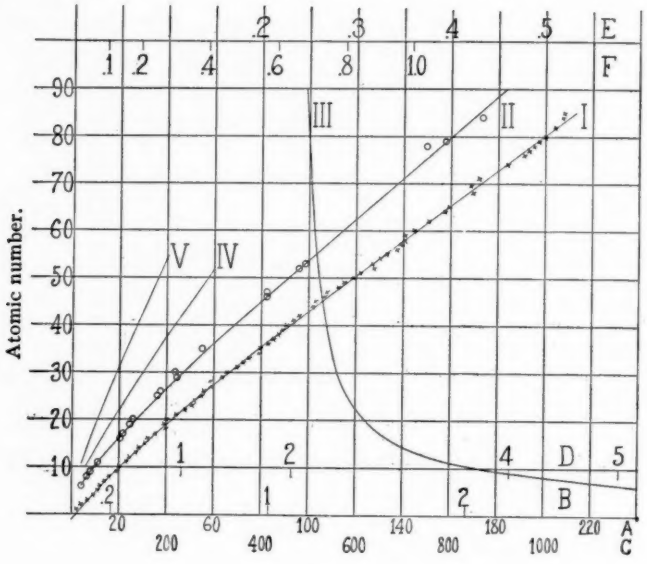

Fig. 2.

Curve I. $\frac{1}{k_1}\sum_P \beta^2$. Scale *A*. Curve I. $\sum_P \beta^2 \times 10^2$. Absolute scale *B*.

Curves II., IV. and V. $\frac{\sqrt{v}}{k_1}\sum_P (a\beta) \times 10^8$. Scale *C*.

Curves II., IV. and V. $\sum_P (a\beta) \times 10^{10}$. Absolute scale *D*.

Curve III. $\frac{1}{\sqrt{v}}\left(\frac{\Sigma\beta^2}{\Sigma(a\beta)}\right) = \left(\frac{\Sigma(a\beta)}{\Sigma a^2} = \frac{\omega_1}{c}\right) \times 10^{-8}$. Scale *E*.

Curve III. $\frac{\omega_1}{c} \times 10^{-8}$. Absolute scale *F*.

There have been cogent reasons for believing that a few so-called "valency" electrons do have these larger orbits, and, if so, electromagnetic theory should still be capable of dealing with the matter as long as they are in the steady state not radiating energy. A more comprehensive method of analysis is required, however, before any equations embracing these outside electrons can be obtained. It seems to be necessary to show that such electrons may be permitted by the theory

without disturbing the equilibrium, on account of their mutual interference and the resulting perturbations produced. The evidence in favor of their existence is greatly strengthened by the very recent work of J. Frenkel[1] in calculating on Bohr's theory the "intrinsic potentials" of, and the Volta contact electromotive forces between, metals and non-metals by means of the supposed existence of a small number of electrons having these large orbits. In the way it is done, it is these large orbits alone that are responsible for the effects, the small ones being of no avail. He also calculates the electrical energy of the quasi-surface condenser thus produced, making it the same as the well-known energy of surface tension, which is thus explained in terms of atomic structure.

It is noteworthy that the order of magnitude of the frequencies in Curve III., 10^{18}, is the same as that of characteristic X-ray frequencies. It has been pointed out before that these frequencies of revolution should not be related directly to these X-ray frequencies. The one may be a function of the other, but the evidence goes to show that the X-ray frequencies are functions primarily of the atomic number and a series of ordinals alone, which would give the smooth character to the Moseley curves. The dependence upon Σa^2, $\Sigma(a\beta)$ and rotation frequency secondarily may account for the small curvature observed in his curves. The large number of lines in the X-ray spectrum is alone almost sufficient to make this independence of the two kinds of frequencies probable.

THE ABSOLUTE VALUES OF THE CONSTANTS.[2]

The curves in Figs. 1 and 2 have abscissæ which are dependent upon the absolute value of the constant k_1, defined by the equations (33) and (11) above. It is necessary to know the value of this constant before Σa^2, etc., can be found in absolute measure. It is possible to find k_1 if we know the number of electrons in any one atom, their arrangement in rings, and their speeds. We shall make a tentative assumption as to the carbon atom, and derive from it the value of k_1. The reason for giving the curves in terms of this constant is so that, if any one prefers a different assumption as to carbon or any other atom, the absolute values may be more readily obtained. Let us take $\Sigma\beta^2$ for carbon as given in the example, equation (26). Then, by (32)

[1] J. Frenkel, On the Surface Electric Double-layer of Solid and Liquid Bodies, Phil. Mag., April, 1917, p. 297.

[2] The following numerical estimates of absolute values must, of course, be considered as tentative and subject to revision. They are chiefly based upon the calculation of actual velocities of electrons in rings according to electromagnetic theory. The process of making such calculations is long and tedious and should be checked both as to method and errors of a mechanical nature. It should be emphasized that the methods outlined here should yield the proper numerical values when these velocities of electrons in rings are accurately known.

$$k_1 = .001438/12 = 1.198 \times 10^{-4}. \tag{36}$$

The value of v, as in (8), is 7.73. Hence, to convert the abscissæ of the curves into absolute measure, multiply those of

Curve I., Fig. 1, for Σa^2 by $k_1 \times 10^{-16}/v = 0.155 \times 10^{-20}$,

Curve I., Fig. 2, for $\Sigma \beta^2$ by $k_1 = 1.198 \times 10^{-4}$,

Curve II., Fig. 2, for $\Sigma(a\beta)$ by $\frac{k_1}{\sqrt{v}} 10^{-8} = 0.431 \times 10^{-12}$,

Curve III., Fig. 2, for $\frac{\Sigma\beta^2}{\Sigma(a\beta)} = \frac{\Sigma(a\beta)}{\Sigma a^2} = \frac{\omega_1}{c}$ by $\sqrt{v} \times 10^8 = 2.78 \times 10^8$.

For the carbon atom the reading from the curve for Σa^2 is 34.95. Multiplying by the factor 0.155×10^{-20} gives in absolute measure $\Sigma a^2 = 5.42 \times 10^{-20}$ sq. cm. Equating this to (24) gives the radius of the outside ring $a = 0.792 \times 10^{-10}$ cm. This absolute value for the radius is in accord with former results, all of which show that the radius is a very small quantity compared with the distance between adjacent atoms. The edge of the tetrahedron in diamond is 2.528×10^{-8} cm., 319 times the radius above determined.

We obtain also the mean angular velocity and frequency of revolution for carbon from (25) to be $\omega = 4.80 \times 10^{18}$, and $n = 0.764 \times 10^{18}$.

Had we made a different assumption for the carbon atom, the order of magnitude of these quantities is not greatly changed. For example, let the carbon atom be supposed to consist of a single ring of six electrons, for which β falls between .00846 and .012, say at .010. The exact value of β for a ring of six has not been calculated at this writing. From this assumption $\Sigma\beta^2 = 6 \times 10^{-4}$, and

$$k_1 = 0.5 \times 10^{-4}. \tag{37}$$

Hence $(k_1 \times 10^{-16})/v = 6.47 \times 10^{-22}$, and $\Sigma a^2 = 6.47 \times 34.95 \times 10^{-22} = 2.26 \times 10^{-20}$ sq. cm., and the radius of the ring $a = .614 \times 10^{-10}$ cm., instead of .792 according to the former assumption. Also $\Sigma(a\beta) = 6a\beta = 3.684 \times 10^{-12}$, and

$$\frac{\Sigma\beta^2}{\Sigma(a\beta)} = \frac{\Sigma(a\beta)}{\Sigma a^2} = \frac{6 \times 10^{-4}}{3.684 \times 10^{-12}} = \frac{3.684 \times 10^{-12}}{2.26 \times 10^{-20}} = 1.63 \times 10^8 = \frac{\omega}{c}. \tag{38}$$

Hence the angular velocity $\omega = 4.89 \times 10^{18}$, about the same as the mean value of ω in the former example.

SPECULATION AS TO THE KIND OF ATOMS IN THE INTERIOR OF THE EARTH.

By means of the absolute values of k_1 in (36) and (37), obtained from different assumptions as to the structure of the carbon atom, we are enabled to get an approximate value of the constant k in the weight

equation (10). For, by (33) $k = 15.96 \times 10^{-22}/k_1$. For the first kind of carbon atom we have

$$k = 13.32 \times 10^{-18}, \tag{39}$$

and for the second

$$k = 31.9 \times 10^{-18}. \tag{40}$$

A knowledge of this constant enables us to find from (11) $\Sigma_E \beta^2$ for the earth, that is, the sum of the squares of β for every electron in the earth. This is

$$\sum_E \beta^2 = \frac{8kr_E^2}{m_0 e^2}, \tag{41}$$

where r_E, the radius of the earth may be taken as 6.367×10^8 cm., and m_0, the mass of the electron, as $.898 \times 10^{-27}$ grams, and $e = 4.77 \times 10^{-10}$ electrostatic units. With the first kind of carbon atom we get

$$\sum_E \beta^2 = 21.12 \times 10^{46} \tag{42}$$

and with the second

$$\sum_E \beta^2 = 50.56 \times 10^{46}. \tag{43}$$

Dividing this by the total number of electrons in the earth, we obtain a value of β for the average electron in the earth. The volume of the earth is 1.083×10^{27} c.c., mean density $5.5247 \pm .0013$, and mass, therefore, 5.984×10^{27} grams.

If we take the number of electrons per atom as proportional to the atomic number, then the number of electrons per gram of any substance is constant. This may be shown as follows. It is well known that a cubic cm. of a perfect gas, under the standard conditions of temperature and pressure, contains the same number of molecules, say N. If d is the density of the gas, then the number of molecules per gram is N/d, since $1/d$ is the volume of a gram of the gas. If M is the molecular weight,

$$M = n_1 A_1 + n_2 A_2 + n_3 A_3 + \cdots,$$

where A_1, A_2, etc., are the atomic weights of the various atoms in the molecule, and n_1, n_2, etc., the numbers of these atoms respectively. If the number of electrons in the atom, P, is proportional to the atomic number or approximately to the atomic weight, we have

$$A_1 = bP_1; \quad A_2 = bP_2, \quad \text{etc.}$$

Hence $M = b(n_1 P_1 + n_2 P_2 + \cdots) = bP$, where P is now the number of electrons in one molecule. It follows that the mass of all the molecules in one c.c. of the gas is $m = \text{vol.} \times \text{density} = d = hNM = kNP$, where h and k are constants. Hence, for two different gases

$$d/d' = P/P'.$$

Since the number of molecules per gram is N/d, the electrons per gram are proportional to NM/d and to NP/d. And, since N is constant, and $P/d = P'/d'$, the electrons per gram are the same for different gases.

The number of electrons per gram is, therefore, the same for all forms of matter, liquids and solids, because the atoms have the same weight in any of these forms, and the number of electrons per atom may be supposed to be the same under all conditions.

Knowing that the number of atoms of hydrogen per gram is 6.05×10^{23} approximately, and considering that the hydrogen atom has but a single electron, this number may be taken as the number of electrons per gram for any substance.

Multiplying the electrons per gram by the mass of the earth in grams gives the total number of electrons in the earth as approximately

$$6.05 \times 10^{23} \times 5.984 \times 10^{27} = 36.2 \times 10^{50}. \qquad (44)$$

The mean values of β^2 and β for the average electron in the earth may now be found by dividing $\Sigma_E \beta^2$ by the total number of electrons, giving, for the twelve-electron carbon atom,

$$\beta^2 = 0.5856 \times 10^{-4} \quad \text{and} \quad \beta = 0.00765.$$

Comparing this value with β for a ring of four electrons, 0.00846, and for a ring of eight, 0.012, shows that it is a little less than the value for the ring of four. Comparing with the values of obtained for hydrogen in its different conditions, namely, 0.00738, 0.00369 and 0.00246, corresponding to the first, second and third states of hydrogen respectively, shows that it is about the same as the value in the first state of hydrogen. The majority of the electrons in the atoms of the earth's crust with which we are acquainted have, according to the Curve I., Fig. 2, a value of β considerably in excess of 0.00765, so that the electrons at the center of the earth must have a value less than the mean. Such a value would be too small to agree with any of the forms of atom except hydrogen. It has been pointed out elsewhere that there is no evidence for the existence of hydrogen in the first state, and that the normal condition for hydrogen is the second state in which $\beta = 0.00369$, which is less than the mean value for the earth. If the interior of the earth were composed of hydrogen, the density might still be very large, as this is due to the compactness, or the interspace between atoms, rather than to the character of the atoms themselves. We know that the density at the center must be in excess of 5.52, the mean value, because the average density of the surface, that of the earth's crust, is considerably less than the mean density.

The above is at least an interesting speculation indicating that we have obtained a method that may eventually yield some information as to the nature of the large body of atoms in the interior of the earth. Had we carried through the calculation based upon the six-electron atom the mean value of β would have been about half again larger than that given.

BULK MODULI.

In a former paper[1] a formula was given by which the bulk modulus of a crystal can be calculated from a knowledge of the forces interacting between the atoms. This may be defined as the ratio of the pressure per sq. cm. in grams weight to the change in volume per unit volume, that is, the substance is more incompressible the greater its bulk modulus. This formula is

$$M = \frac{\sqrt{3}}{9 \times 981} \frac{1}{l^2} \frac{dF}{dl}.$$

Table III. gives the values of M for several crystals as calculated by this formula. The measured values of those that are known are given in the third column, together with some crystals for which the modulus has not been calculated, in order to show the great range of measured values for different crystals, as well as to show that the order of magnitude of the range of calculated values is the same.

The calculated values are larger in every instance where the value has been measured, indicating a more incompressible substance than it is measured to be. The range of values among those calculated is about six to one from greatest to least, while the range of the measured values is 66 to one. The measured value for tourmaline is well toward the top of the list of calculated substances, showing the same order of magnitude.

Measurements of the bulk modulus must be subject to considerable error because we have no means of compressing a substance except to press upon it with another substance having a similar character. In such a case it is difficult to say that the two substances do not interpenetrate each other to a certain extent at the surface at least. By exerting pressure by mercury upon a piece of steel, for example, Bridgeman has shown that it is possible to force the mercury completely through the steel, so that, when broken afterwards, it shows an amalgamated surface over the entire break. If any interpenetration whatever occurs it will have the effect of reducing the value of the bulk modulus obtained, which is in line with the results shown in the table. Moreover, if the same substance is used to produce the compression for a number of different substances, the amount of such interpenetration should vary widely with the kind

[1] Loc. cit.

of space lattice of the crystal. Hence, great variations in measurements should be anticipated if there occurs any interpenetration, which is again in agreement with the results in the table.

TABLE III.

Crystal.	Bulk Modulus.	
	Calculated.	Measured.
Altaite, PbTe	$21{,}700\times10^6$	
Diamond, C	17,520 "	
Galena, PbS	15,300 "	
Fluorspar, CaF_2	11,330 "	860×10^6
KI	8,380 "	
AgBr	7,660 "	
KBr	7,380 "	
Zincblende, ZnS	6,500 "	
Iron Pyrites, FeS_2	5,470 "	906 "
AgCl	4,400 "	
Rock Salt, NaCl	4,380 "	246 "
KCl	4,000 "	138 "
Melaconite, CuO	3,660 "	
Manganblende, MnS	3,570 "	
Barite		535 "
Beryl		1,384 "
Quartz		387 "
Topaz		1,694 "
Tourmaline		9,140 "

If the same crystal were measured with compressing substances which vary as widely as possible in their properties, it might prove to be the case that different values of the bulk modulus would be obtained for the same crystal, which would help to confirm the above suggestions.

REVIEW AND SUMMARY.

1. The problem of finding the average mechanical force that one electrical charge exerts upon a second charge, each being in uniform circular motion, has been solved, both for the form of electromagnetic equations originally proposed by Thomson, and for the more recent form of Lorentz involving retarded potentials. It was shown in a former paper that the Lorentz form without modification cannot be applicable to the electrons in the atoms of matter, because their application would produce a force, varying inversely as the square of the distance between two pieces of matter at a great distance apart, more than 10^{30} times greater than the existing force of gravitation. When, however, the result thus obtained

is multiplied by a factor proportional to the kinetic energy of the electron itself, the attraction agrees very closely with that of gravitation. When such a factor is introduced into the Lorentz equations the average force, at the distances considered in crystals, reduces to very nearly the same form whether the Lorentz or the original Thomson equations are used, the same within a factor of 2 in some of the terms in r^{-4}. This is regarded as some justification for using the original Thomson equations for these ranges of distance. The equation for the force between two atoms, derived from these equations as given in a former paper, is here applied to twenty crystals belonging to the cubic system.

2. Equilibrium conditions are derived for several forms of space lattice. In each of them the only unknown quantities are $\Sigma_P a^2$ and $\Sigma_P (a\beta)$, summed for each electron in the atom concerned, a being the radius of its orbit, and β its speed in terms of the velocity of light.

3. Some hypothesis is required before either the relative or the absolute values of a and β, the unknown quantities pertaining to the atoms, can be found. In a former paper the equal moment of momentum hypothesis for each and every electron in the atoms was adopted for the lack of something better. This hypothesis led to certain serious difficulties, in that it demanded that in such crystals there should be double atoms instead of single atoms at each point of the space lattice. The evidence of the spectrometer has made this view untenable.

4. The hypothesis as to the atoms adopted in this paper, instead of the equal moment of momentum hypothesis, is that $\Sigma_P \beta^2$ is constant for any given atom. A former work has indicated that the gravitational attraction between bodies at a distance is proportional to the product of the sum of the squares of the speeds of the electrons summed over each body separately. Since the weight of an atom is constant, it is reasonable to suppose in view of the above that the sum of the squares of the speeds of the electrons within it is constant.

5. This hypothesis avoids the difficulties in which the equal moment of momentum hypothesis involved us, by which $\Sigma_P(a\beta)$ is constant for a given atom. According to the new "$\Sigma_P \beta^2$ = a constant" hypothesis, the same atom may take two or three different forms without altering $\Sigma_P \beta^2$. This means that the moment of momentum is not constant, but may have two or three different forms corresponding to changes in the radii.

6. The values of $\Sigma_P a^2$, $\Sigma_P (a\beta)$ and $\Sigma_P \beta^2$ have been found for each of twenty different atoms that enter as many different crystals, and are plotted as curves in Figs. 1 and 2, against the atomic number in terms of a constant multiplier. If an assumption is made as to some one form of atom, these constants may be determined and the above values found for

any atom in absolute measure. The assumption that must be made concerns the number of electrons in some atom and the speed of each; but, fortunately, the radii of their orbits is not required. It is also fortunate that the speed of electrons in rings has been previously determined numerically for a ring of 4 and a ring of 8 electrons. These speeds come out independent of the radius of the ring, and dependent only upon the number in the ring. The carbon atom has been selected in making this assumption, and two forms of it are given as examples, a 12 electron, and a 6 electron atom. The values of the constants do not differ greatly for the two supposed forms of carbon. By means of this an absolute scale has been determined in Figs. 1 and 2. It is there given for the twelve atom assumption.

7. Two secondary curves, II. and III., Fig. 1, are given as the alternative values of $\Sigma_p a^2$ for some atoms. These curves have abscissæ $1/2^{4/3}$ and $1/2^{8/3}$ of those in Curve I. respectively. The value of $\Sigma_p a^2$ for the atoms O, S, Cl and Br may occur in crystals in any one of two or three forms, their weights remaining the same, but their radii changing. This change in the radius does not affect $\Sigma_p \beta^2$. Not more than two of these forms occur in the crystals considered in case of the above elements, but it is predicted that the third form will appear in some crystals not yet studied. For example, sulphur occurs in zincblende, manganblende and iron pyrites with a value corresponding to Curve II., and in galena with a value corresponding to Curve III., and no crystal gives a value corresponding to the principal Curve I. On the other hand, chlorine in NaCl, KCl, and bromine on KBr give values on the Curve I., and in AgCl and AgBr in Curve II., but no value in the crystals studied falls on Curve III. for these elements.

8. Curve II., Fig. 2, with the secondary Curves IV. and V. give the values of $\Sigma_p (a\beta)$, proportional to the total moment of momentum of the atom. These three curves have abscissæ in the ratios $1 : 2^{2/3} : 2^{4/3}$ and they respresent the alternative values that an atom of sulphur, for example, may possess in different circumstances. These curves are nearly straight lines for atomic numbers above 40, and, were it not for the alternative values in these three curves, would give good reason to suppose that the moment of momentum for each electron is nearly constant.

9. Curve III., Fig. 2, gives the average value of ω/c for each atom, from which the average frequency of revolution may be obtained. According to it, the average frequency approaches a nearly constant minimum for the heavier elements, but may be very large for the lightest element, hydrogen.

10. A proof is given to show that the curve for $\Sigma_p a^2$ in Fig. 1 is in good

agreement with the theory that atoms may be formed in rings in a plane as in the Meyer figures, the volume of the enclosing sphere increasing by equal steps for the addition of each electron, but this offers no explanation for the two alternative values for the same atom corresponding to Curves II. and III.

11. According to the twelve-electron-atom-assumption the radius of the outside ring of eight is determined in centimeters to be 0.792×10^{-10}. This is 1/319th part of the edge of the elementary tetrahedron in the diamond. According to the six electron assumption it is 0.614×10^{-10} cm. The mean frequency of revolution is about $.76 \times 10^{18}$ in both examples, that is, the order of magnitude of characteristic X-ray frequencies.

12. A knowledge of absolute values leads to a determination of the constant in the equation for the weight of an atom, from which $\Sigma_E \beta^2$ for all the electrons in the earth is found to be 21.12×10^{46}. Dividing this by the total number of electrons in the earth, which is equal to the mass of the earth in grams times the electrons per gram, a constant quantity, namely $5.984 \times 10^{27} \times 6.05 \times 10^{23} = 36.2 \times 10^{50}$, the value of β^2 for the average electron in the earth is $.585 \times 10^{-4}$, and $\beta = 0.00765$. This result leads to a speculation that the interior of the earth may be hydrogen, or, at any rate, the very lightest of the known elements. That a result, found in such a manner comes out within the range of the possible values of β for any atoms helps to strengthen the theory that the gravitational force is proportional to $\Sigma\beta^2$. It is, at least, an interesting speculation because it suggests for the first time a possibility of finding the kind of elements that make up the interior of the earth and possibly other heavenly bodies.

13. From the mechanical forces interacting between the atoms in a crystal a formula for the bulk modulus was derived in a former paper, which is here applied to several crystals. A comparison with measured values in Table III., in the few cases where measurements are known, shows that the crystals are invariably more incompressible according to calculation than they are measured to be, although the order of magnitude of the two results corresponds. It is suggested that the great variation in the measured values among different crystals shows a certain degree of interpenetration of the compressing substance and the substance compressed. This would always have the effect of reducing the apparent incompressibility, in the direction that the measurements indicate. New measurements of these quantities may well be made, employing the same crystal with different compressing substances. If different values are then obtained, the fact may be attributed to different degrees of interpenetration. Liquids, however, which have no space lattice formation may

act very much alike. If the compressing substance were a solid it would be better.

14. The derivation of the force equations from the cubic space lattice formation is given in an appendix so as to interfere less with the continuity of the argument. A section of this is devoted to a consideration of the error that is made in neglecting the more distant atoms in the crystal than those included in a cube of edge four times the elementary cube. This error is appreciable but not excessively great, as indicated by calculating the total force due to all atoms along selected radii in the crystal to an infinite distance. The chief effect of such error is to alter somewhat the values of the constants d, v and u in the equilibrium conditions (5), (8) and (9) for different lattices. But, the fact that we obtain good curves in Figs. 1 and 2 from different crystals and different lattices goes to show that there is not a great error in these constants due to the omission of atoms more distant than those calculated.

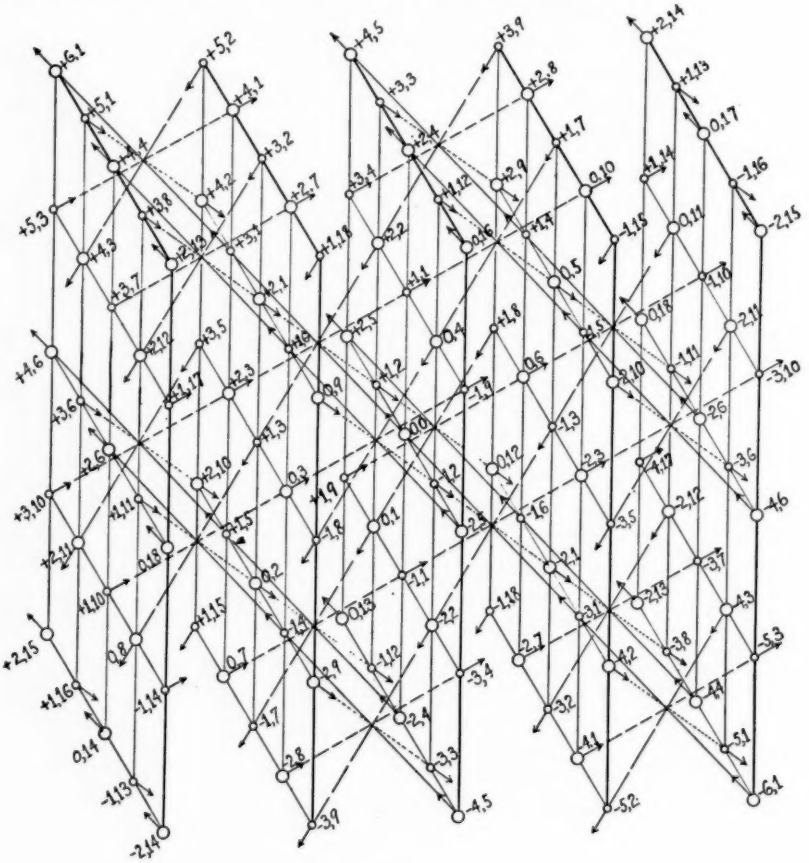

Fig. 3.

TABLE IV.

Plane. No.	Atom. No.	x.	y.	z.	r.	l.	m.	n.	α.	Cos α.	Sin α.	+ Direction of Axis. x.	y.	z.
−6	1	0	0	$-2\sqrt{3}l$	$2\sqrt{3}l$	0	0	−1	0	+1	0	—	—	0, +6−1
−5	1	$+\frac{1}{3}\sqrt{6}l$	"	$-\frac{5}{3}\sqrt{2}l$	$3l$	$+\frac{1}{3}\sqrt{6}$	"	$-\frac{5}{9}\sqrt{3}$	109° 28′.3	$-\frac{1}{3}$	$+\frac{2}{3}\sqrt{2}$	0, 12	0, 14	"
"	2	"	"	"	"	"	"	"	"	"	"	0, 8	0, 16	"
"	3	"	"	"	"	"	"	"	"	"	"	0, 10	0, 18	"
−4	1	$-\frac{1}{3}\sqrt{6}l$	"	$-\frac{4}{3}\sqrt{3}l$	$\sqrt{6}l$	$-\frac{1}{3}$	"	$-\frac{2}{3}\sqrt{2}$	"	"	"	"	"	"
"	2	"	"	"	"	"	"	"	"	"	"	0, 12	0, 14	"
"	3	"	"	"	"	"	"	"	"	"	"	0, 8	0, 16	"
"	4	$+\frac{2}{3}\sqrt{6}l$	"	"	$2\sqrt{2}l$	$+\frac{1}{3}\sqrt{3}$	"	$-\frac{1}{3}\sqrt{6}$	0	+1	0	0, 12	0, 14	"
"	5	"	"	"	"	"	"	"	"	"	"	0, 8	0, 16	"
"	6	"	"	"	"	"	"	"	"	"	"	0, 10	0, 18	"
−3	1	0	"	$-\sqrt{3}l$	$\sqrt{3}l$	0	"	−1	"	"	"	—	—	"
"	2	"	$-\sqrt{2}l$	"	$\sqrt{5}l$	"	$-\frac{1}{5}\sqrt{10}$	$-\frac{1}{5}\sqrt{15}$	109° 28′.3	$-\frac{1}{3}$	$+\frac{2}{3}\sqrt{2}$	0, 8	0, 16	"
"	3	"	+ "	"	"	"	+ "	"	"	"	"	0, 12	0, 14	"
"	4	"	− "	"	"	"	− "	"	"	"	"	0, 10	0, 18	"
"	5	"	+ "	"	"	"	+ "	"	"	"	"	0, 8	0, 16	"
"	6	"	− "	"	"	"	− "	"	"	"	"	0, 12	0, 14	"
"	7	"	+ "	"	"	"	+ "	"	"	"	"	0, 10	0, 18	"
"	8	$+\sqrt{6}l$	0	"	$3l$	$+\frac{1}{3}\sqrt{6}$	0	$-\frac{1}{3}\sqrt{3}$	"	"	"	0, 12	0, 14	"
"	9	"	"	"	"	"	"	"	"	"	"	0, 8	0, 16	"
"	10	"	"	"	"	"	"	"	"	"	"	0, 10	0, 18	"
−2	1	$+\frac{1}{3}\sqrt{6}l$	"	$-\frac{2}{3}\sqrt{3}l$	$\sqrt{2}l$	$+\frac{1}{3}\sqrt{3}$	"	$-\frac{1}{3}\sqrt{6}$	"	"	"	0, 12	0, 14	"
"	2	"	"	"	"	"	"	"	"	"	"	0, 8	0, 16	"
"	3	"	"	"	"	"	"	"	"	"	"	0, 10	0, 18	"
"	4	$+\frac{2}{3}\sqrt{6}l$	"	"	$2l$	$+\frac{1}{3}\sqrt{6}$	"	$-\frac{1}{3}\sqrt{3}$	0	+1	0	0, 7	0, 15	"
"	5	"	"	"	"	"	"	"	"	"	"	0, 9	0, 17	"
"	6	"	"	"	"	"	"	"	"	"	"	0, 11	0, 13	"
"	7	$-\frac{2}{3}\sqrt{6}l$	$+\sqrt{2}l$	"	$\sqrt{6}l$	$-\frac{2}{3}$	$+\frac{1}{3}\sqrt{3}$	$-\frac{1}{3}\sqrt{2}$	109° 28′.3	$-\frac{1}{3}$	$+\frac{2}{3}\sqrt{2}$	0, 10	0, 18	"
"	8	"	− "	"	"	"	− "	"	"	"	"	"	"	"
"	9	"	+ "	"	"	"	+ "	"	"	"	"	0, 12	0, 14	"
"	10	"	− "	"	"	"	− "	"	"	"	"	"	"	"
"	11	"	+ "	"	"	"	+ "	"	"	"	"	0, 8	0, 16	"
"	12	"	− "	"	"	"	− "	"	"	"	"	"	"	"
−2	13	$+\frac{1}{3}\sqrt{6}l$	0	"	$2\sqrt{3}l$	$+\frac{2}{3}\sqrt{2}$	0	$-\frac{1}{3}$	0	+1	0	0, 12	0, 14	"
"	14	"	"	"	"	"	"	"	"	"	"	0, 8	0, 16	"
"	15	"	"	"	"	"	"	"	"	"	"	0, 10	0, 18	"
−1	1	$-\frac{1}{3}\sqrt{6}l$	"	$-\frac{1}{3}\sqrt{3}l$	l	$-\frac{1}{3}\sqrt{6}$	"	$-\frac{1}{3}\sqrt{3}$	109° 28′.3	$-\frac{1}{3}$	$+\frac{2}{3}\sqrt{2}$	"	"	"
"	2	"	"	"	"	"	"	"	"	"	"	0, 12	0, 14	"
"	3	"	"	"	"	"	"	"	"	"	"	0, 8	0, 16	"
"	4	$+\frac{2}{3}\sqrt{6}l$	"	"	$\sqrt{3}l$	$+\frac{2}{3}\sqrt{2}$	"	$-\frac{1}{3}$	0	+1	0	"	"	"
"	5	"	"	"	"	"	"	"	"	"	"	0, 10	0, 18	"
"	6	"	"	"	"	"	"	"	"	"	"	0, 12	0, 14	"
"	7	"	$-\sqrt{2}l$	"	$\sqrt{5}l$	$+\frac{2}{15}\sqrt{30}$	$-\frac{1}{5}\sqrt{10}$	$-\frac{1}{15}\sqrt{15}$	109° 28′.3	$-\frac{1}{3}$	$+\frac{2}{3}\sqrt{2}$	0, 8	0, 16	"

Plane. No.	Atom. No.	x.	y.	z.	r.	l.	m.	n.	a.	cos a.	sin a.	+ Direction of Axes. x.	y.	z.
−1	8	$+\frac{2}{3}\sqrt{6}l$	$+\sqrt{2}l$	$-\frac{1}{3}\sqrt{3}l$	$\sqrt{5}l$	$+\frac{2}{15}\sqrt{30}$	$+\frac{1}{5}\sqrt{10}$	$-\frac{1}{15}\sqrt{15}$	109°28′.3	$-\frac{1}{3}$	$+\frac{2}{3}\sqrt{2}$	0,8	0, 16	0, +6−1
"	9	"	− "	"	"	"	− "	"	"	"	"	0,10	0, 18	"
"	10	"	+ "	"	"	"	+ "	"	"	"	"	"	"	"
"	11	"	− "	"	"	"	− "	"	"	"	"	0, 12	0, 14	"
"	12	"	+ "	"	"	"	+ "	"	"	"	"	"	"	"
"	13	$-\frac{1}{3}\sqrt{6}l$	$+2\sqrt{2}l$	"	$3l$	$-\frac{1}{5}\sqrt{6}$	$+\frac{2}{3}\sqrt{2}$	$-\frac{1}{9}\sqrt{3}$	"	"	"	"	"	"
"	14	"	− "	"	"	"	− "	"	"	"	"	0, 10	0, 18	"
"	15	"	+ "	"	"	"	+ "	"	"	"	"	0, 8	0, 16	"
"	16	"	− "	"	"	"	− "	"	"	"	"	0, 12	0, 14	"
"	17	"	+ "	"	"	"	+ "	"	"	"	"	0, 10	0, 18	"
"	18	"	− "	"	"	"	− "	"	"	"	"	0, 8	0, 16	"
0	1	0	$+\sqrt{2}l$	0	$\sqrt{2}l$	0	− 1	0	"	"	"	"	"	"
"	2	"	+ "	"	"	"	+ "	"	"	"	"	0, 12	0, 14	"
"	3	"	− "	"	"	"	− "	"	"	"	"	0, 10	0, 18	"
"	4	"	+ "	"	"	"	+ "	"	"	"	"	0, 8	0, 16	"
"	5	"	− "	"	"	"	− "	"	"	"	"	0, 12	0, 14	"
"	6	"	+ "	"	"	"	+ "	"	"	"	"	0, 10	0, 18	"
"	7	$-\sqrt{3}l$	0	"	$\sqrt{6}l$	− 1	0	"	"	"	"	"	"	"
"	8	+ "	"	"	"	+ "	"	"	"	"	"	0, 8	0, 16	"
"	9	− "	"	"	"	− "	"	"	"	"	"	0, 12	0, 14	"
"	10	+ "	"	"	"	+ "	"	"	"	"	"	0, 10	0, 18	"
"	11	− "	"	"	"	− "	"	"	"	"	"	0, 8	0, 16	"
"	12	+ "	"	"	"	+ "	"	"	"	"	"	0, 12	0, 14	"
"	13	$+2\sqrt{2}l$	"	"	$2\sqrt{2}l$	"	"	"	0	+1	0	0, 13	0, 8	"
"	14	"	"	"	"	"	"	"	"	"	"	0, 14	0, 9	"
"	15	"	"	"	"	"	"	"	"	"	"	0, 15	0, 10	"
"	16	"	"	"	"	"	"	"	"	"	"	0, 16	0, 11	"
"	17	"	"	"	"	"	"	"	"	"	"	0, 17	0, 12	"
"	18	"	"	"	"	"	"	"	"	"	"	0, 18	0, 7	"

APPENDIX.

In the case of the diamond lattice the coördinates of position of the surrounding atoms, with respect to a selected atom at the origin of the coördinates, were given[1] in Table I., page 264. In a similar manner the following Table IV. gives them for a simple cubic lattice like that of rock salt. The atoms are numbered as in the diagram Fig. 3.

The calculation of the numerical values of the functions f_4 and f_6, given in equations (1) and (2) above, has been carried out for each of the 124

[1] Loc. cit.

atoms surrounding the central atom in a cube of edge $4l$, giving the results in Table V. Each atom in the (x, y) or $z = 0$, plane gives $F_z = 0$ because n is a factor of (1) for these atoms, and is zero in the plane $z = 0$.

TABLE V.

Odd Planes.

Plane.	Atoms.						
-1.....	1, 2, 3.	$F_z = e^2\{+0.57735 \sum_P (a\beta) \sum_{P'} (a\beta) l^{-4} - 5.052 \sum_P a^2 \sum_{P'} a^2 l^{-6} \cdots\} k.$					(45)
"	4, 5, 6.	"	"	+0.203703	"	+0.27778	" (46)
"	7–12.	"	"	+0.0413	"	−0.0974	" (47)
"	13–18.	"	"	−0.02165	"	+0.005846	" (48)
-3.....	1.	"	"	−0.166667	"	+0.277778	" (49)
"	8, 9, 10.	"	"	−0.021395	"	+0.00891	" (50)
"	2–7.	"	"	0.000000	"	−0.05385	" (51)
-5.....	1, 2, 3.	"	"	−0.01136	"	−0.0126	" (52)
Sum of odd planes....		"	"	+0.6013	"	−4.6455	" (53)

Even Planes.

-2.....	1, 2, 3.	$F_z = e^2\{-0.66375 \sum_P (a\beta) \sum_{P'} (a\beta) l^{-4} + 0.8625 \sum_P a^2 \sum_{P'} a^2 l^{-6} \cdots\} z.$					(54)
"	4, 5, 6.	"	"	+0.10821	"	−0.03375	" (55)
"	7–12.	"	"	−0.02838	"	+0.0667	" (56)
"	13–15.	"	"	+0.01273	"	+0.00434	" (57)
-4.....	1, 2, 3.	"	"	+0.0960	"	+0.0529	" (58)
"	4, 5, 6.	"	"	−0.009569	"	−0.016445	" (59)
-6.....	1.	"	"	−0.0104125	"	+0.0043402	" (60)
Sum of even planes..		"	"	−0.49517	"	+0.94059	" (61)
Sum of odd and even planes.....		"	"	+0.1061	"	−3.7049	" (62)

The forces in the Table V. are given for the negative planes only, those on one side of the central atom, thus including but one half of the cube of edge $4l$. In this form of lattice it happens that each atom is a center of symmetry, not only for the position and kind of atom, but for the direction of its axis of rotation as well. It always happens that there is an atom of chlorine in rock salt, for example, having its axis parallel to a corresponding atom of chlorine at an equal distance on the opposite side of the selected atom. Equation (1) shows that the force that one pair of such atoms exerts upon the selected atom is zero irrespective of the value of l. The force changes sign if we reverse the signs of l, m and n, the direction cosines, a remaining the same. The size of the space lattice is, therefore, indeterminate if we consider the whole cube. This makes it possible to impose a second condition before the size of the lattice is fixed. This is, that we must obtain the same value of l whether we

select a sodium or a chlorine atom upon which to figure the force. We get the same value of l by equating to zero the total force of all the sodium atoms in one half the cube, acting upon a selected chlorine atom, or by equating to zero the total force of all the chlorine atoms in one half the cube acting upon a selected sodium atom. Since the odd planes always contain atoms of the opposite kind from the selected atom, it is concluded that the equilibrium condition for all crystals like rock salt is obtained by equating (53), which is the same as (6) to zero.

DEGREE OF APPROXIMATION.

Had we included in the calculation the innermost cube only, of edge $2l$, we should have had for the odd planes only the forces given in (45), (46) and (49), and for the even planes only (54), giving the results

$$\text{Odd planes,} \quad F_z = e^2\{+ 0.6144\sum_P(a\beta)\sum_{P'}(a\beta)l^{-4} - 4.4964\sum_P a^2\sum_{P'}a^2l^{-6}\cdots\}k, \quad (63)$$

$$\text{Even planes,} \quad F_z = e^2\{- 0.66375\sum_P(a\beta)\sum_{P'}(a\beta)l^{-4} + 0.8625\sum_P a^2\sum_{P'}a^2l^{-6}\cdots\}k, \quad (64)$$

which may be compared directly with (53) and (61) above. The inclusion of the next outlying cube of atoms makes less difference here in the case of the odd planes than in that of the even. But, the question arises how much the results in (53) and (61), which have been used in the paper, would be changed if we had included more of the outlying atoms. This question can not be answered exactly until such calculations are made. They involve considerable labor and have not been carried out beyond the cube of edge $4l$, so that it is very desirable to obtain some kind of an estimate of the error made in neglecting the more distant atoms. To help give some idea of this error the forces due to all the atoms lying along certain radii to infinity have been obtained in the case of the even planes (61), which showed the greater difference when the outer cube was included.

For example, along the radius vector from the origin to atom $(-6, 1)$ we come to atoms of the same kind and with axes parallel to the atom at the origin at equal intervals, the second being twice, and third three times as far, and so on, as atom $(-6, 1)$, the force of which is given by (60). Since the first term varies as r^{-4}, we may use this equation to find the force of all other atoms along this radius to infinity. This is equivalent to multiplying (60) by the sum of the series to infinity

$$2^{-4} + 3^{-4} + 4^{-4} + 5^{-4} \cdots = 0.082323,^{1}$$

to obtain the coefficient of the fourth power term due to all other outlying atoms along this radius. Similarly, for the sixth power term, we have to sum the series

$$2^{-6} + 3^{-6} + 4^{-6} + 5^{-6} \cdots = 0.017343.$$

This result would have made equation (60), if we include all atoms along this radius to infinity, have the coefficient of l^{-4} − 0.0008565, and of l^{-6} 0.0000755, different from that given in (60).

In a similar manner all atoms along several different radii have been included, giving the following amounts to be added to the coefficients as given in the Table V.

Direction of Radius.	Coef. of l^{-4}.	Coef. of l^{-6}.
(−6, 1)	−0.0008565	0.0000755
(−2, 4) (−2, 5) (−2, 6)	0.008903	0.0005853
(−4, 4) (−4, 5) (−4, 6)	0.0007875	0.0002852
(−2, 1) (−2, 2) (−2, 3)	0.00969	0.001240
(−4, 1) (−4, 2) (−4, 3)	0.001425	0.00007606
Sum	0.001006	0.00052106

When these values are added to the coefficients in (61), it changes the fourth power coefficient by about one part in five hundred, and the sixth power by about one part in two thousand. The atoms added by this process do not include all, even in the next adjacent cube with edge $6l$, but these figures indicate that we can not rely upon the accuracy of the figures in the Table V. in the third decimal place in the fourth power coefficient, and it is not now possible to say whether the value will turn out to be larger or smaller than those in (61), if we were to include all surrounding atoms to a great distance. The preceding, however, may be regarded as showing something as to the order of the error made by omitting outlying atoms at greater distances.

The Diamond Lattice.

The diamond form of lattice consists of two interpenetrating face-centered lattices. If we number the (111) planes consecutively, from 0 for the selected atom as before, the even planes in one of the lattices are symmetrical with respect to the selected atom, giving a total force of zero irrespective of the size of the lattice. The odd planes are not symmetrical with respect to it, and the force must be calculated for all odd planes, both positive and negative since these do not cancel each

[1] For a table of the sums of these series, see De Morgan's Calculus, p. 552.

other. In the case of ZnS the planes alternate, even planes being zinc and odd sulphur, if we select a zinc atom on which to figure the force. The equilibrium condition must be the same whether we select a zinc or a sulphur atom upon which to figure the force as in the case of rock salt.

The crystal CaF_2 has a structure similar to ZnS in some respects. If Ca is substituted for Zn and one of the F's for S, the arrangement so far is the same. The Ca planes recur at regular intervals, this interval being the altitude of the tetrahedron on the elementary triangular base in the Ca plane. One of the F planes occurs at one quarter of this distance above the Ca plane, similar to the S in ZnS, and the other F at the same distance below the Ca plane, which has no corresponding plane in ZnS. The spacing of the planes then gives the following regular succession

F–Ca–F–Space–F–Ca–F–Space–F–Ca–F–Space and so on,

there being three planes at regular intervals and then one missing. From this it is evident that if we select a Ca atom upon which to figure the force, the positive planes will just balance the negative planes, thus making the size of the lattice indeterminate. For the equilibrium condition, therefore, we do not need to figure the force upon a calcium atom. The case is different if we select one of the F atoms, for, then the Ca atoms are not symmetrical about it. On the other hand, the F atoms are symmetrical about it. This narrows the condition down to precisely the same formula as applies to the diamond or zincblende, because we only have to take into account the force of all the Ca atoms upon a fluorine atom.

AN EXPERIMENTAL INVESTIGATION OF THE TOTAL EMISSION OF X-RAYS FROM CERTAIN METALS.

BY C. S. BRAININ.

THE experiments described in this paper were undertaken with the purpose of studying the integral intensity of the emission of x-rays by metals from two standpoints: (1) The variation of the intensity of the radiation from a given metal with the voltage and (2) the dependence of the intensity upon the atomic weight (or number) of the metallic radiator at different voltages. It seemed that the use of the Coolidge cathode and the gas-free x-ray tube gave opportunity for the maintenance of unchanging conditions such as it was hitherto impossible to obtain with the gas-filled tube. Moreover, beside this important consideration, the data upon which rest our ideas of the dependence of the total energy of emitted rays upon the voltage and the atomic weight do not seem to be founded upon experiment sufficiently extensive to preclude the desirability of further investigation upon this important topic.

The experiments upon which has been based a relation between the total intensity of x-rays emitted by a metal and the voltage across the electrodes of the tube are mainly those of Whiddington and Beatty. Their results are in agreement with the conclusion reached by Sir J. J. Thomson.[1] His theoretical investigation, founded upon certain atomic assumptions and upon the Stokes ether pulse or stopped electron hypothesis, brought him to the relation that the intensity of the x-rays produced by the collisions of electrons and atoms should be proportional to the fourth power of the velocity of the moving electrons. It should be proportional, therefore, also to the square of the difference of the potential impressed upon the electrodes of the tube. Furthermore, the results of the above mentioned experimenters in conjunction with those previously obtained by Kaye seemed to indicate that under like conditions of current and voltage the emission of two metals is very nearly directly proportional to their atomic weights. Both these results are summed up in the equation

$$E = KAP^2, \qquad (1)$$

where K is a constant, A the atomic weight of the radiating target and P

[1] Phil. Mag., June, 1907.

the difference between the electrodes of the x-ray tube. Recently Bergen Davis[1] has deduced this formula, basing his development upon the quantum hypothesis of radiation and assuming the x-rays to emanate from the atom itself and not from the impacting electron. Equation (1) is to be taken as applying only to the general or independent (non-characteristic) x-radiation. It is then in place to examine the experimental evidence so far brought forward in favor of this very broad formula.

Whiddington[2] makes the statement in an article on the "Production of Characteristic Roentgen Radiations" that "it comes out that E (per unit cathode ray current) is nearly proportional to the fourth power of the velocity." No experimental data connected directly with this question could be found in any of his papers. At best he was getting primary x-rays from one metal (silver) only; his range of voltages was from 7 to 21 kilovolts. His studies on the other metals were made with secondary rays produced by the primary rays from the silver anticathode. Beatty[3] used a method which was quite direct; he measured the total ionization produced in a chamber which absorbed completely the x-rays that entered it at the voltages used by him. His range was from 8.5 to 21 kilovolts and he investigated four metals, rhodium, silver, copper and aluminum. For the voltages used he found that rhodium, silver and aluminum held well to the voltage square law; his results for copper show a large increase at a voltage approximately corresponding to the critical voltage for the characteristic K-radiation from copper but hardly justify the acceptance of a straight line relation up to this critical voltage. In the case of aluminum the entire voltage range is of course above the critical voltage for its K-radiation. Rutherford[4] took up this question after the appearance of the Coolidge cathode and used a regular (commercial) tungsten target x-ray tube. He compared the emissions at three voltages, 48, 64, and 96 kilovolts and found that though the radiated energy was very nearly proportional to the square of the voltages, at the highest voltage the ratio was perceptibly greater.

As to the other factor contained in the equation (1), the atomic weight A, the direct evidence in its favor is again mainly the above-mentioned paper of Beatty and the work of Kaye.[5] Beatty found that the emissivity of rhodium and silver as well as that of aluminum were in the correct ratio in spite of the fact that the critical voltage for the K-radiation of the latter had been exceeded. Kaye studied the emission of a great many

[1] PHYS. REV., Jan., 1917.
[2] Roy. Soc. Proc., 85 A, 1911.
[3] Proc. Roy. Soc., 89 A, 1913–14.
[4] Phil. Mag., Sept., 1915.
[5] Phil. Trans. Roy. Soc., 209 *A*, 1908–9.

metals and found that upon partially screening out the soft (characteristic?) rays the intensity of the remaining rays was approximately proportional to the atomic weights. This work was done at a voltage of about 25,000. No attempt was made to obtain complete absorption of the rays in the ionization chamber. However, the experiments certainly show the preponderance of the atomic weight as a factor in determining the emissivity of the substances at a given voltage. It is also interesting to note here that for voltages from 1,500 up to 3,500 volts Whiddington[1] found that no connection existed at all between emission and atomic weight.

A third point of interest which necessarily comes out in study of the variation of the x-ray emission with voltage is the behavior of the metals when the critical voltage for the appearance of the characteristic rays is reached. With the exception of aluminum as noted above in Beatty's paper, all the metals thus far studied, whose critical *K*-voltages lay within the experimental range, show a sharp increase in emissivity when these rays are excited.

The Experiments.

A great difficulty attended the choice of substances for these experiments, as it was badly limited by the necessity of having the element in metallic form and of having the temperature of fusion high enough to withstand the great heating to which they would be subjected. Finally the following six were chosen, so as to obtain the greatest range of atomic weights, and used throughout the work: Platinum, tungsten, silver, molybdenum, copper and cobalt. In order that the intensity of ionization might truly represent the intensity of emission a total absorption of the x-rays which, at any voltage, entered the chamber, was desired and provision for it made as described below. To avoid appreciable absorption of the x-rays in the wall of the bulb, it was planned to have the rays pass only through a very thin window of mica, before entering the ionization chamber so that the effect of this absorption could be neglected even at low voltages.

Description of Apparatus.—Fig. 1 gives a diagrammatic view of the very simple apparatus used. The Coolidge cathode, *C*, was mounted in a horizontal and the anti-cathode, *A*, in a vertical position. The target itself consisted of a brass block 2.5 cm. high and of hexagonal cross-section, to each facet of which a different metal was attached by means of tiny screws at top and bottom. As the little rectangular metallic targets were of different thicknesses, the brass block was trimmed down so that

[1] Roy. Soc. Proc., 1911 *A*, 85, p. 99.

all the surfaces were at the same distance from the center. Into the base of the brass block was set one end of a narrow brass tube to which a bar of soft iron was fastened, making a right angle with the tube. This tube slipped over an aluminum rod, set up vertically in the x-ray bulb until an iron pin, which was affixed to the upper end of the aluminum rod, touched the inside of the brass block and thus provided a pivot for the latter's rotation. The soft iron bar was cut in two places and hinged there so that it could be folded up along the brass tube and the whole

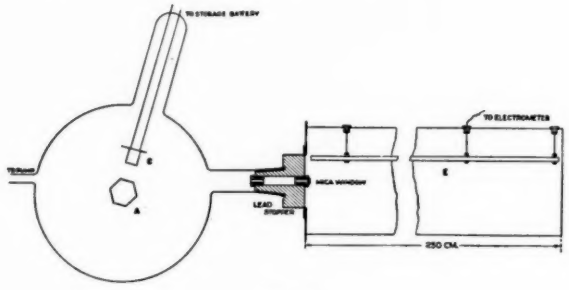

Fig. 1.

passed into the x-ray bulb through a wide glass tube fused in at the top. When this rotating target had been properly slipped over the aluminum rod, the wings of the soft iron bar were unfolded and the wide glass tube entrance sealed off. The adjustment had previously been made so that the centers of the surfaces of the target came opposite the cathode itself. The anti-cathode could now be rotated from without the tube by means of an electro-magnet. A mirror and a small sighting tube with cross-hairs were used to insure the turning of the surfaces so that the x-rays measured would come off each surface under like conditions. The figure shows the position of the target with respect to the cathode and the path into the ionization chamber.

The x-rays passed only through a mica window of thickness .001 cm. before entering the ionization chamber. This thin sliver of mica was fastened with De Khotinsky cement to a small lead plug which itself was cemented to the large lead stopper. This in turn fitted into a glass tube fused to the x-ray bulb, the end of which was slightly flared. The lead and the glass were carefully fitted and cemented together. The whole had been previously adjusted so that the channel for the x-rays through the lead pointed toward the area from which the rays were to come. The holes through the small lead plugs were .18 cm. in diameter and had been so calculated that the radiation would traverse the length of the ionization chamber without coming in contact with the side walls. The

axis of the ionization chamber had to coincide with the axes of the holes through the lead in order to effect this and the proper adjustments were made before the apparatus was assembled.

The ionization chamber itself consisted of a thin-walled steel tube of outside diameter 10 cm. and length 250 cm. This was used as a grounded electrode; the other electrode (E, Fig. 1) was a lead pipe stiffened by an iron rod within it which ran the entire length of the chamber. It was suspended inside the steel tube from four amber plugs, one of which carried a wire connection out to the electrometer. It was finally decided to use a Braun electrometer with an aluminum needle and measure the rate of leak over a definite range of 500 volts. The needle was always charged so as to indicate over 1,500 volts and the time was taken between 1,500 and 1,000 volts. As no readings were made with the difference of potential between the electrodes less than 1,000 volts, saturation conditions at all times were obtained in the tube. The electrometer needle showed no tendency to stick and gave results which agreed well with one another. The natural leak was practically always a negligible quantity. Proper heavy lead shielding was placed around the x-ray bulb to prevent effects in the electrometer due to secondary or reflected rays.

The x-ray bulb was evacuated with a mercury condensation pump of the Langmuir type made entirely of glass after a design by Prof. G. B. Pegram; it was used in conjunction with an oil fore-vacuum pump and gave extremely rapid service. A freezing-out chamber was fused in between the pump and the x-ray bulb and was kept immersed in a mixture of salt and ice. This served to keep the mercury vapor pressure in the bulb low enough to prevent the formation of a gas discharge. It took several days of alternate pumping and running of the discharge to remove the occluded gases and to make the bulb serviceable for the experiment; but once it had reached a satisfactory state it was found necessary to do but little pumping and several days of observations in succession were sometimes possible without any need of using the pump. In spite of the three De Khotinsky seals, made under difficult conditions, there was at no time a real leak perceptible and most of the runs of observations were made with the pump in readiness but not in actual use. Early in the stage of preparation of the tube it was filled with hydrogen and when this had been nearly all pumped out again a discharge was run for some time with the anti-cathode acting as a cathode. This served to clear perfectly the surfaces of the metal targets, some of which had become slightly oxidized.

The current for heating the tungsten filament of the cathode came from a storage battery placed upon a carefully insulated glass support. Four

six-volt $2\frac{1}{2}$ ampere batteries were used, two parallel sets, each composed of two batteries in series, giving twelve volts. The electronic current through the x-ray tube was measured by means of a Weston milliammeter reading directly to tenths of a milliampere. One terminal of this meter was connected to the anticathode and the other grounded. A strip of tinfoil, which was grounded, was fastened around the x-ray tube near the connection of the anticathode and the milliammeter so as to intercept any possible leak over the surface of the glass and thus prevent it from being registered on the ammeter. The main circuit high potential current was obtained from a transformer fed by a 500-cycle, 150-volt alternator. The current from this was rectified by a kenotron system. A very large condenser was placed in parallel in the circuit so that the voltage could be relied upon to be constant and the current unidirectional. The middle of the transformer was grounded. The voltages were measured by means of a spark gap between spheres 12.5 cm. in diameter.

Method.—The data taken in these experiments were obtained in two distinct ways:

1. With a given metal acting as target the voltage was varied by small steps and the rates of the electrometer leak measured; in this way the ionization produced by the energy in the x-ray output of a particular metal could be obtained as a function of the voltage.

2. Keeping the conditions of the voltage and current constant, the different metal targets could one after another be subjected to the bombardment of the electrons and the relative intensities of the emission of x-rays for any particular voltage could be obtained. This was done for a great number of different voltages throughout the range found possible with the apparatus.

The lower limit of usable voltages is naturally determined by the amount of energy necessary to produce readable leaks on the electrometer in a reasonable length of time. It was found impossible to use such high currents through the tube as are possible with the tungsten Coolidge tubes prepared by the General Electric Company. A current over 5 milliamperes soon broke down the vacuum even at very low voltages. The upper limit in an experiment of this nature depends upon how far the voltage can be raised and practically total absorption still be obtained in the ionization chamber. This is really best determined from the results themselves and the shape of the curves obtained by the above method (1) is the best guide as to how high a voltage can be used.

In order to increase the absorption of x-ray energy in the chamber, it was planned to use some dense vapor and the experiments were begun with the chamber containing air saturated with ethyl bromide vapor.

However, the study of certain phenomena which were found and are hereinafter described made it desirable to have the air alone present, in order to avoid the great increase in ionization which takes place in the vapor when the x-rays absorbed by it contain wave-lengths which correspond to the characteristic K-radiation from one of the component elements of the gas. These would begin to appear, of course, when the voltage across the tube is equal to the critical voltage for the excitation of this radiation. This increased ionization is entirely out of proportion to the increased energy of the x-radiation due to the increased voltage alone, and difficult to correct for. With the long ionization chamber containing only dry air it was found that the highest voltage at which the results could be relied upon was in the neighborhood of 33,000 volts. Above 35,000 volts there appeared on all the curves a sudden great increase due to the impinging of a large amount of the ionization upon the end wall of the chamber. Tests with an electroscope showed that no appreciable amount of x-ray energy remained unabsorbed below that voltage. The lowest it was found possible to use was 4,700 volts, though in general the readings were taken above 7,000 volts.

During the progress of the experiments the first x-ray tube set up became so blackened that its further use was very difficult and at approximately the same time the glass pump cracked at one of its fused joints. The whole apparatus was, therefore, taken down; the pump was repaired and a new tube set up differing only in slight details from the former one. Data were then obtained on the metals which had not been examined and much of the data already obtained was carefully gone over. It was found that while the actual quantitative data differed by a constant factor, the general results remained exactly the same.

EXPERIMENTAL RESULTS.

I.

In the results presented below in the form of curves, the energy, as represented by the rate of leak of the electrometer reduced to unit electron current, through the x-ray tube, is plotted as ordinate and the square of the voltage used is plotted as abscissa. If the resulting curve is a straight line pointing to the origin, the energy of emission is really proportional to the square of the voltage as expressed by the equation (1). A deviation from the straight line passing through the origin and before the critical voltage for the characteristic radiation is reached necessarily means a failure of the equation to represent truly the phenomenon.

Platinum and *tungsten*, the two metals of highest atomic weight in the list and the only two whose critical voltage for the L-radiations are within

the range of the experiments, show a similarity in that they both deviate from the " square of the voltage " law. It is to be noticed particularly that these curves do not become straight lines through the origin until the voltage of 22,000 volts, approximately, has been reached in the case of platinum, and 19,000 volts, approximately, in the case of tungsten. It is to be noticed also that for a short interval of voltage the radiation of tungsten seems to be more powerful than that of platinum, a fact which is brought out again later in connection with the results from method (2).

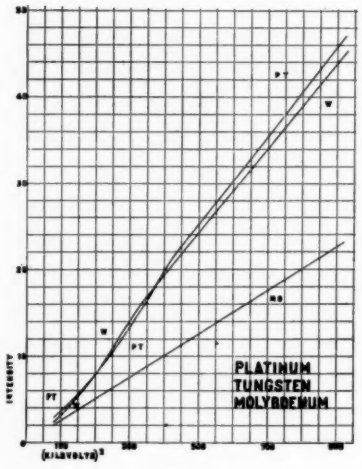

Fig. 2.

Molybdenum, as shown on Fig. 2, seems to hold well to the law for the range of voltages given and, not only that, but also appears not to deviate from this law upon the voltage reaching and passing the critical voltage for its characteristic K-radiations. For molybdenum this is about 20,000 volts. All the curves on Fig. 2 are mean curves based on a number of separate sets of observations on each metal.

Copper and *cobalt* also show a striking similarity in behavior and they are plotted together in Fig. 3. Especially in the case of copper is it possible to say that a straight line really represents the data up to the point where the curvature, due to the characteristic, begins to be noticeable. For cobalt also the curve may be said to be fairly close to a straight line. The critical voltage for cobalt is about 10,000 volts; that for copper is 11,000 volts very nearly. Upon approaching these voltages both curves bend gradually upward and show what we may be allowed, for the sake of brevity, to call a striking increase of " efficiency." This increase is greater for the metal of lower atomic weight, cobalt, at least within the range of the experiment.

The results for silver are shown separately in Fig. 4. The upper curve was obtained with the air in the ionization chamber saturated with ethyl bromide vapor, the other with air alone, without this vapor. Upon plotting the very first results obtained with silver, when the chamber still contained the vapor, and calculating the ratios between the ionization intensities and the squares of the voltages, the writer was surprised to find the slight downward break in the curve as shown in the figure, upon reaching the vicinity of the critical voltage for the silver K-characteristic

radiations, 25,000 volts. Up to this point the curve is surely a straight line pointing toward the origin. To make certain of the real existence of this phenomenon, the data for silver were taken several times alternately with data for metals already examined, copper, platinum and molybdenum. In each case the results were a repetition of the data previously obtained. Then the ethyl bromide vapor was removed from the ionization chamber and dry air only used as absorber. The curve of the results

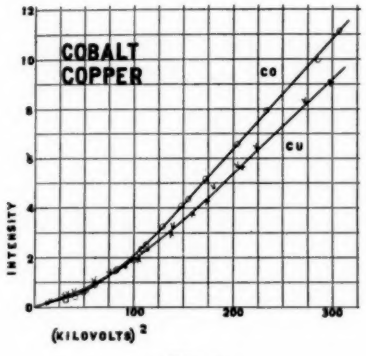

Fig. 3.

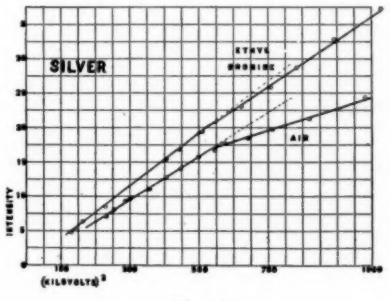

Fig. 4.

so obtained shows the break much more prominently. The lessening of the effect in ethyl bromide vapor was no doubt due to the reaching of a voltage greater than the critical voltage for the K-characteristic radiations from the bromine atoms in the vapor. This voltage is about 17,000. In this case the increase in relative ionization power served to mask partly the decrease in the so-called efficiency of the silver radiating mechanism. Nothing could be found in the apparatus to explain away the anomaly, which would not apply equally well to the other metals by which, however, it was not shown. Beatty and Whiddington had not found this phenomenon because their highest voltages were below the voltage at which it appeared.

II.

The results obtained from the second experimental procedure are given in Fig. 5 below. The actual voltages and not the voltage squared are here used as abscissæ; the ordinates represent the ratio that the emission energy of the particular metal bears to the emission of molybdenum at the given voltage. Molybdenum was chosen as the unit of reference because it gave (in Fig. 2 above) the straight-line relation between voltage squared and emission intensity postulated by the formula $E=KAP^2$ and was therefore best suited to show deviations from this relation. Its own emissivity is naturally then represented by a straight line of unit

ordinate. For a better understanding of the data presented by the curves, a table is added giving the atomic numbers and weights and their ratios to those of molybdenum.

TABLE I.

Metal.	At. Wt.	Ratio of At. Wt.	At. No.	Ratio of At. No.
Pt.....	195	2.17	78	1.86
W.....	184	1.92	74	1.72
Ag.....	107	1.10	47	1.12
Mo.....	96	1.00	42	1.00
Cu.....	63	.66	29	.69
Co.....	59	.62	27	.64

Examination of Fig. 5 brings out some interesting information and further confirmation of some of the results discussed above. The deviation of platinum and tungsten from proportionality in their emission intensity to atomic weight (or number) is very striking. If they really obeyed this relation exactly, the curves representing each would be a straight line parallel to the voltage axis and to the line representing molybdenum and at the proper distances from these. However, at the lowest voltage shown, 4,700, the relative emission is very much below this and it rises rapidly with the voltage, becoming actually the required straight lines in the neighborhood of 20,000 volts. At this stage the ratio of the emission of platinum to that of molybdenum, from the curve, is about 2.06 and that of tungsten about 1.93, which is closely in proportion to the atomic weights. Again there is a short interval of voltages where tungsten is a better radiator than platinum. We might also, perhaps, call attention to the fact that tungsten seems to reach the straight line relation before platinum and that the voltages at which this is reached are very roughly twice the critical voltages for their respective characteristic *L*-radiations.

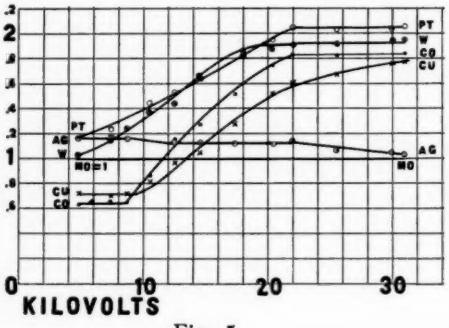

Fig. 5.

Silver appears to give an amount of radiation which is very slightly out of proportion to its atomic weight at the lower voltages, but falls pretty well into line above 10,000; at the lowest voltages its emissivity is as high as that of platinum and higher than that of tungsten. This

was to be expected if silver maintains the straight-line relation between emission and voltage squared, but the slight apparent rise with respect to molybdenum itself cannot, of course, be thus accounted for. The decrease of the ratio for silver above 22,000 volts is a further confirmation of the curious downward break in the curve for this metal as shown in Fig. 4. Between these two changes the ratio to the emission of molybdenum is 1.13 nearly.

In the case of copper and cobalt the results are fairly well given by straight lines parallel to the molybdenum unity line until the appearance of the characteristic *K*-radiation energy. They both then increase rapidly, crossing the curves for molybdenum and silver, finally appearing to approach a limiting value, and do not increase indefinitely in relative emissivity. In the region below the critical voltages for their *K*-rays, the average of the ratios of their emissions to molybdenum are .71 for copper and .64 for cobalt, which is in good agreement with the values in the table. The constant ratio of 1.83, to which cobalt rises after 20 kv., has no easily interpretable meaning.

III.

Three distinct modes of behavior on the part of the metals, when the voltage is reached which corresponds to their critical voltages for the *K*-rays, have so far been discovered:

1. Most elements increase rapidly in the " efficiency " of their radiated energy output which is evidenced by a break upward, when the plotting of the curves is made, as in this paper; such substances are copper, iron, selenium, nickel, zinc, etc., which have already been studied, and cobalt which this paper adds to the list.

2. Aluminum was found early to be an exception in that it seemed to show no such break at all but gives evidence that it continues on in an unbroken straight line; as mentioned at the beginning of this article, Beatty bases part of his confirmation of the law of proportionality of emission to atomic weight upon the fact that aluminum maintains this relation throughout the range of his experiments. Molybdenum may also now be added to aluminum as an example of such behavior.

3. The behavior of silver, which decreases in " efficiency," with the appearance of its characteristic *K*-radiations.

It seems to the writer that the different modes of behavior recited above are rather antagonistic to the theory that independent and characteristic rays come from different sources of radiation. It has been sometimes held that the former are sent out from the impacting electron and the latter from the electrons of the impacted atom, in a similar way probably

as the line radiation of the visible spectrum. One may then attempt to explain away the aluminum and molybdenum behavior by saying that the characteristic radiations in the case of these metals do not contain relatively as much energy as, for example, the characteristics of copper; and it is possible that a very slight increase of energy may go unnoticed in such experiments as these. On the other hand, the characteristic radiation from both aluminum and molybdenum have been found to be not at all weak. However, the one example of silver, unless refuted by later work, makes the above theory unlikely; for it would be rather difficult to understand why the energy emission from the impacting electron should not continue in proportion to the fourth power of the velocity. It seems to make it probable that the entire radiation comes from the atomic radiating structure itself, and, furthermore, that the reaction of this mechanism is not parallel in all atoms when their respective critical voltages are reached. The behavior of the independent radiations in the neighborhood of the characteristic lines of rhodium, as found by D. L. Webster[1] may be perhaps taken as a support in this direction.

SUMMARY.

1. A study has been made of the total intensity of the x-ray emission from the six metals, platinum, tungsten, silver, molybdenum, copper and cobalt over a range of voltages extending from about 5,000 volts to about 33,000 volts. The relations between the energy radiated and the voltage and between the energy and the atomic weight were investigated; this includes a test of the validity of the equation $E = KAP^2$.

2. Below 20,000 volts approximately the energy radiated by platinum and tungsten was found not to be proportional to A and P^2; above this voltage, however, it was in agreement with the above equation.

3. Molybdenum obeyed this relation throughout the range of voltages, and showed no deviation from this relation when the voltage was increased above the critical voltage for the K-radiation.

4. Copper and cobalt seemed to obey this relation below their critical voltages for the K-radiations, but above those voltages their emission increased *more rapidly* than is required by the "voltage squared law."

5. Silver also obeyed this law below the critical voltage for its characteristic K-radiation, but above that voltage the emission energy increased *less rapidly* than is required by the "voltage squared law."

In conclusion I desire to express my sincerest thanks to Prof. Bergen Davis who suggested the problem and whose kindly interest was a continual source of help and encouragement.

PHOENIX LABORATORY,
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[1] PHYS. REV., June, 1916.

THE DIFFUSION OF ACTINIUM EMANATION AND THE RANGE OF RECOIL FROM IT.

BY L. W. MCKEEHAN.

INTRODUCTION.

THE diffusion of actinium emanation, and the distribution of the active deposit to which it gives rise, have been the subjects of numerous researches.[1] In no case, however, has the experimental arrangement been simple enough in its geometry to permit easy calculation of the distribution to be expected on the basis of the known phenomena of gaseous diffusion and of radioactive recoil. In the work here reported this simplicity has been of prime consideration. Values of the diffusion coefficient and of the range of recoil in air have been obtained.

APPARATUS.

The essential features of the apparatus are shown in Fig. 1, which represents two sectional views through the vertical axis of the diffusion space. Two similar brass plates, A, A, are held at either of two fixed

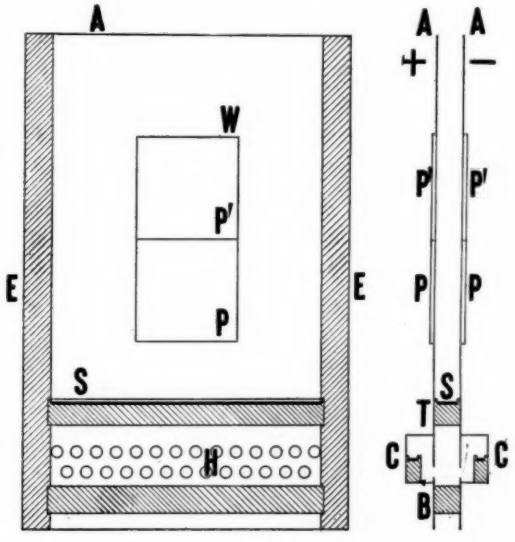

Fig. 1.

[1] W. T. Kennedy, Phil. Mag. (6), 18, 744, Nov., 1909. J. C. McLennan, Phil. Mag. (6), 24, 370, Sept., 1912. H. P. Walmsley, Phil. Mag. (6), 26, 381, Sept., 1913. A. N. Lucian, Phil. Mag. (6), 28, 761, Dec., 1914.

distances apart by the three strips of ebonite, E, E, and B, and maintained at a suitable difference of potential (usually 200 volts) by a battery of lead accumulators. The source of emanation, S, is a uniform layer of an actinium preparation spread in the trough, T (which forms a false bottom of the diffusion space, adjustable in height), or in two similar troughs fixed in the side boxes, C, C. When the latter are in use the trough T is, of course, removed entirely, and the emanation enters the diffusion space through the holes, H. The square collecting plates, P, P', are four in number, two filling the windows, W, in each plate, A. Their inner surfaces are flush with that of A, and they are flanged on the outside to prevent leakage of the diffusing emanation at their edges.

The pressure in the diffusion space is adjusted by placing the whole apparatus in a bell-jar of large volume containing some P_2O_5 and connected to a suitable pump and MacLeod gauges. Conditions of pressure and temperature are maintained constant for a time in excess of five hours, so that radioactive equilibrium will be practically attained between the emanation and its products. The pressure is then changed quickly to atmospheric and the bell-jar removed, these operations requiring about thirty seconds. The four plates, P, P', are then all removed at once, and their activities measured in an α-ray electroscope of such dimensions that the full ranges of the α-rays of AcC_1, and AcC', are utilized. From these activities the activities in the preceding steady state are computed, using $\lambda_B = 3.18 \times 10^{-4}$ sec^{-1} for the transformation constant of AcB. This value of λ_B was checked many times during the experiments.

TABLE I.

Essential Dimensions of Apparatus, in Centimeters.

Collecting plates, $h \times w$	4.00×4.00
Width of diffusion space	11.0
Thickness of Diffusion space, s	0.50 or 1.00
Depth of surface of source below lower edge of P	0.64, 4.64, or in side boxes.
Height of A above upper edge of P'	4.0

THEORY.

The assumptions made as the basis of the following theory fall into three classes. The first comprises those that depend upon the construction and use of the apparatus, and that can therefore be realized to any desired degree of approximation. These are as follows: a steady state of diffusion and decay is obtained; the plates are unlimited; the diffusion is linear in the region to be considered; the electric field between the plates is sufficient to insure saturation with respect to the charged atoms of AcA; the activity computed from the measurements is proportional to the total quantity of AcB on the plate in the steady state.

The second class of assumptions comprises the applications of well-established physical laws to the phenomena discussed and these are acceptable at least to the accuracy attained in the experiments. They are as follows: the diffusion coefficient is independent of the concentration of emanation atoms and the degree of ionization of the air, but is inversely proportional to the air pressure; the recoil atoms formed from the emanation all have the same range, which is inversely proportional to the air pressure; the direction of recoil is random; the effect of the applied electric field upon the path of recoil is negligible; atoms of AcA, regardless of their charge, are adsorbed by any solid surface which they may reach by recoil or by diffusion.

The third class of assumptions is composed of the hypotheses suggested by the present study or aribtrarily introduced for the sake of simplifying the theory. Each of these will be criticized in the discussion of the experimental results. They are:

1. Only emanation is supplied by the source.
2. The path of recoil is a straight line.
3. The variation of the concentration of emanation atoms within a distance equal to the range of recoil is negligible.
4. The recoil atoms formed from the emanation are all positively charged at the end of recoil.
5. The decay of AcA and the growth of AcB takes place without changing the relative number of atoms on opposing areas of the two plates.

Referring again to Fig. 1, take the origin of coördinates at the middle of the lower edge of the lower positive collecting plate, measure x upward on the positive plate, and y perpendicular to it. The distance between the plates being s, the planes $y = 0$ and $y = s$ are the positive and negative plates respectively.

The volume concentration of emanation atoms is a function of x only and in the steady state is

$$\rho_x = \rho_0 e^{-\sqrt{(\lambda p/D_1)}x},$$

where λ is the transformation constant of the emanation, D_1 its coefficient of diffusion in air at unit pressure, and p the pressure. Then a number of atoms $\lambda\rho_x$ will, on the average, decay per second per unit volume at (x, y), and the recoil atoms formed may strike either plate or be stopped in the gas, depending upon the values of y and of the range R_1/p (where R_1 is range at unit pressure), and upon the direction of recoil.

If a sphere of radius R_1/p is drawn with its center at (x, y), the number of recoil atoms received per second on either plate by direct recoil from unit volume at (x, y) will be equal to

$$\lambda\rho_x \frac{\text{area of segment of sphere cut off by plate considered}}{\text{total area of sphere}} = \lambda\rho_x \frac{\text{height of segment}}{\text{diameter of sphere}}.$$

Thus the positive plate will receive by direct recoil

$$\lambda\rho_x \frac{\frac{R_1}{p} - y}{2\frac{R_1}{p}} = \lambda\rho_x \frac{R_1 - py}{2R_1} \qquad \text{if } y < \frac{R_1}{p},$$

and

$$0 \qquad \text{if } y > \frac{R_1}{p}.$$

The negative plate will receive all the rest, either by direct recoil, or by the aid of the electric field, after a recoil ending between the plates.

Considering all values of x and y and the conditions of radioactive equilibrium, the surface concentration of recoil atoms in the steady state at the point $(x, 0)$ on the positive plate will be

$$\sigma_{x,\,0} = \rho_x \int_0^s \frac{R_1 - py}{2R_1}\, dy,$$

in which only positive values of the integrand can be taken, and at the point (x, s) on the negative plate will be

$$\sigma_{x,\,s} = \rho_x \left\{ s - \int_0^s \frac{R_1 - py}{2R_1}\, dy \right\}$$

with the same restriction upon the integration.

The total activity on the two lower plates of height h and width w will be

$$A = kws \int_0^h \rho_x dx,$$

where k is a proportionality factor, and that on the two upper plates,

$$A' = kws \int_h^{2h} \rho_x dx = Ae^{-\sqrt{(\lambda p/D_1)}h};$$

therefore

$$\frac{A}{A'} = e^{\sqrt{(\lambda p/D_1)}h},$$

and

$$\log_e\left(\frac{A}{A'}\right) = h\sqrt{\frac{\lambda p}{D_1}}.$$

The fraction of the total activity on the positive plates will be

$$f = \frac{\sigma_{x,\,0}}{\sigma_{x,\,0} + \sigma_{x,\,s}} = \frac{1}{s}\int_0^s \frac{R_1 - py}{2R_1}\,dy.$$

Performing the integration we get

$$f = \frac{1}{2} - \frac{ps}{4R_1} \qquad \text{if } p < \frac{R_1}{s},$$

$$f = \frac{1}{4} \qquad \text{if } p = \frac{R_1}{s},$$

and

$$f = \frac{R_1}{4ps} \qquad \text{if } p > \frac{R_1}{s}.$$

Experimental values of A/A' and of f for a series of values of p and s should afford a basis for calculating D_1 and R_1 and the constancy of these quantities would be a partial confirmation of the theory.

EXPERIMENTS AND DISCUSSION.

Preliminary experiments showed that the distribution on the plates was practically independent of the potential difference for pressures up to atmospheric and for potential differences in excess of 120 volts, so

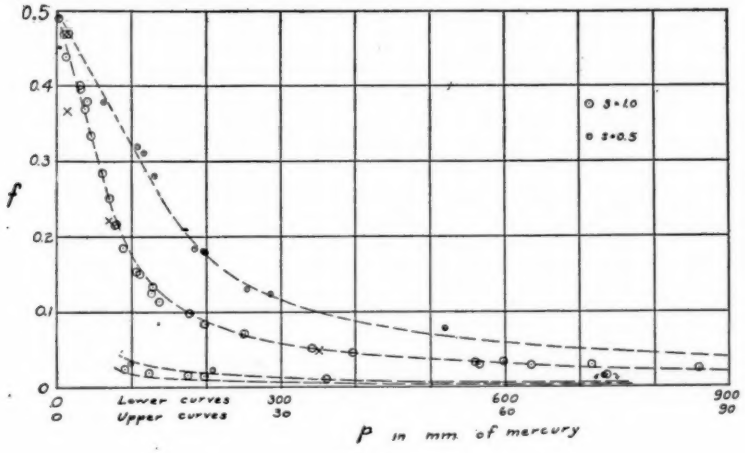

Fig. 2.

200 volts was used throughout. Calculation shows that at pressures below 55 mm. of mercury, 90 per cent. of the positively charged atoms of *AcA* left nearest the positive plate will, for this value of the field, have time to reach the negative plate before they change to *AcB*, so most of the experiments were performed at much lower pressures than this, the lower limit reached being 0.3 mm. The probable error in a single experiment is least at a pressure of about 10 mm. of mercury, but is within a few per cent. throughout the range of pressure used.

To base calculations on the value of f, it was necessary to show that in the absence of an electric field the opposing plates receive the same amount of active deposit. This was rendered difficult by the fact that the electric fields due to small differences of contact potential between portions of the same plate, or of opposite plates, makes the distribution quite irregular when the intense applied field is removed. This irregularity was small immediately after careful cleaning of brass collecting plates but increased with time unless the surface was protected from chemical action (probably oxidation). Lacquered brass plates, and pure gold plates cleaned by a sand blast proved permanently satisfactory in this respect.

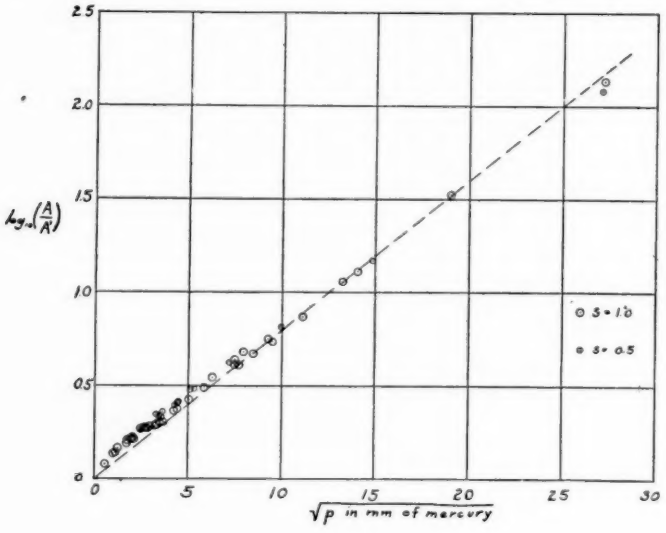

Fig. 3.

The results obtained for f as a function of p, and for $\log (A/A')$ as a function of $\sqrt{p}$, are shown in Figs. 2 and 3 respectively, a point on each figure being obtained in each experiment.

TABLE II.

Summary of Experiments Used in Figs. 2 and 3.

Number of experiments	49
" " " with $s = 1.0$	36
" " " " $s = 0.5$	13
" " " " brass plates	27
" " " " lacquered brass plates	14
" " " " gold plates	8
" " " " source 0.64 cm. below plates	25
" " " " " 4.64 cm. " "	8
" " " " " in side chambers	16

In Fig. 2 the best theoretical curves based on the same value of R_1 are shown as broken lines, the value of R_1 chosen to fit the experiments being 7.0 cm., from which the value of the range in air at normal pressure and the mean temperature of the experiments, 20°.7, would be .0092 cm.

In Fig. 3 the straight line through the origin represents the theoretical relation for $D_1 = 83$, or for the coefficient of diffusion into air at normal pressure $D_1/760 = .109$.

A study of the curve for log (A/A') shows that there is a disturbing factor operating at the lowest pressures, causing a relative increase of activity on the lower plates. This is attributed to the diffusion from the source of other members of the actinium series besides the emanation, that is, to a failure of assumption (1). Such an effect has been noted by other experimenters[1] and it was here found to be much more noticeable when no field was applied, showing that some at least of this stray material left the source while charged, perhaps by recoil from radio-actinium. To prove that the field applied in the neighorhood of the source had the principle effect on purifying the diffusing stream, one of the plates A was divided into two parts by a horizontal ebonite strip, the upper part containing the collecting plates. An electric field in the lower part of the diffusion space was then found to make log (A/A') the same as if the entire diffusion had taken place in the electric field. The nature of the disturbance produced by this stray material shows that its quantity diminishes more rapidly with distance from the source than the possible values of λ and D_1 would allow for an uncharged gas.[2] The easy adsorption of the atoms of a normally solid product, especially if carrying electric charges, is believed a sufficient explanation of this apparent discrepancy, but the behavior of this material will be studied farther in a different apparatus.

The curves for f agree quite well with the theoretical curves, but the nature of the discrepancies indicates that the calculated range at unit pressure would be higher at lower pressures, and for closer approach of the collecting plates at the same pressure. A more serious difficulty is met on examining assumption (3) in connection with the values of R_1 and D_1 derived above, since it is found that this assumption fails at pressures considerably above the lower limit actually reached, and that the curve for f should be much lower at low pressures than the simpler theory indicates. A few computations have been made taking account

[1] L. Wertenstein, Ann. de Phys. (9), 1, 347, April; 393, May, 1914 (in case of radium emanation and products, also refers to previous work).

[2] Excluding AcA, for which λ is far too great.

of the actual variation in the concentration of emanation with the distance from the source. The calculations are tedious, since

$$f = \frac{\int_0^{R_1/p} du \int_0^{2\pi} d\theta \int_{\cos^{-1}(s/u)}^{\pi/2} \{\sin\phi \cos\phi e^{(-\sqrt{\lambda p/D_1R_1}u \sin\phi \cos\theta}\} d\phi}{\int_0^s dy \int_0^{2\pi} d\theta \int_{\cos^{-1}[(s-y)p/R_1]}^{\cos^{-1}(-yp/R_1)} \{\sin\phi e^{(-\sqrt{\lambda R_1/D_1 p}) \sin\phi \cos\theta}\} d\phi + 2\int_0^{R_1/p} du \int_0^{2\pi} d\theta \int_{\cos^{-1}(s/u)}^{\pi/2} \{\sin\phi \cos\phi e^{(-\sqrt{\lambda p/D_1R_1}u \sin\phi \cos\theta}\} d\phi}$$

(only real limits for integration being allowable).

Although one of the integrations in one of the integrals can be performed the resulting form is so badly adapted to valuation by quadrature that all six integrations had to be effected by that means.

Three such calculated values of f are shown by crosses in Fig. 2 and refer to the same conditions as the lower broken line.

The agreement between the experiments and the approximate theory now becomes a matter for explanation, and it is suggested that a moderate tortuosity in the paths of the recoil atoms (*i. e.*, abandonment of assumption (2)) would revalidate the approximate theory by making it improbable that many atoms could reach their full range at low pressures even if projected parallel to the plates. This would also raise the apparent range at low pressures by making a greater proportion of all recoil atoms reach the plates than would be expected on the hypothesis of straight line recoil. Experiments by C. T. R. Wilson's method are in progress to detect if possible whether photographs of recoil trails will show that such a tortuosity exists.

A partial failure of assumption (4) would help to explain the observed results, and this at first sight seems plausible, since the rate of acquirement of the positive charge by the recoil atom has been shown to depend upon the gas pressure.[1] Since, however, the whole number of collisions during recoil probably depends very little upon the pressure, the final condition should be independent of that variable, and the values of f at high pressures indicate that few recoil atoms are then uncharged, even when the chances of so-called initial recombination are the best. That there is some increase in recombination at high pressures is indicated clearly by the high values of f at pressures above 100 mm. of mercury (Fig. 2).

In this connection the high value for the fraction of the recoil atoms uncharged, which was obtained by Lucian[2] with much greater applied

[1] L. Wertenstein, C. R., 161, 696, Dec. 6, 1915.

[2] Loc. cit.

potentials, is to be noted. It is due, no doubt, to the fact that the full range of all the α-particles emitted by the collected deposit was not used; partly on account of the dimensions of the measuring apparatus, and partly on account of the concavity of one of the collecting surfaces. Saturation with respect to the active deposit atoms was also very difficult to obtain in the cylindrical apparatus employed, as the author himself observes. Under these unfavorable conditions his value for the fraction of all recoil atoms which appeared to be uncharged at atmospheric pressure, was 5.1 per cent., which would correspond to a value of f, in the notation of the present paper, approximately equal to 0.025 whereas the value of f here found at this pressure was only 0.015. The disagreement is slightly greater if account is taken of the fact that the ratio of volume to surface in the diffusion space was greater in Lucian's experiments than in these. If there had been no initial recombination, however, the value of f for s equal to one centimeter would have been only 0.002 at atmospheric pressure, so the two results agree better with each other than either does with the hypothesis that such recombination is negligible.

The remaining assumption open to criticism, (5), is that the efficiency of recoil of AcB from the collecting plates is low. The effect of any failure of this assumption would be to increase again the value of f, especially at low pressures, and thus to assist in explaining the agreement between the experiments and the first theory proposed above. The efficiency of recoil from a sanded surface is certainly low.

The experiments of Kennedy[1] on the diffusion of emanation between circular charged plates at various pressures and separations show several of the effects here studied, and even give approximately the same value of R_1 (6.2 cm.), when his data is treated in the same way. The results on diffusion coefficient are not directly comparable. The value here obtained for this constant is, however, about the same as that found by earlier investigators.[2] No satisfactory explanation for the large value obtained, in comparison with that to be expected from the high molecular weight that the emanation must certainly possess, seems as yet available, except the probability that the inert atom of emanation has a weaker stray electric field than the complicated molecules of comparable weight on which the extrapolation of Graham's Law has been based.

[1] Loc. cit.

[2] Kaye and Laby, Tables, 103, 1911.

CONCLUSION.

The laws of ordinary gaseous diffusion and of radioactive recoil suffice to explain the principal effects observed in connection with the diffusion of, and deposit from actinium emanation. The range of recoil from this emanation in air at normal pressure and at 20.7° C. is about .0092 cm. (± 2 per cent.), the diffusion coefficient under the same conditions is about .109 (± 2 per cent). Further work on some disturbing causes is proposed.

I take great pleasure in thanking my colleagues, especially Dr. J. T. Tate, for suggestions and constructive criticism throughout the course of this investigation.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
June 14, 1917.

THE PRESSURE INCREASE IN THE CORONA.

BY EARLE H. WARNER.

I. INTRODUCTION.

IT has been reported by Farwell and Kunz that at the instant the corona appears about an axial wire in a cylindrical tube, the pressure of the gas in the tube suddenly increases.[1] It has always been stated that this pressure increase could not be due to heat, because of the instantaneous character of its appearance, and because of the rapidity with which it disappears as soon as the potential is removed from the wire. Since the only theories which have been advanced to explain the corona assume it to be an ionization phenomenon, it seemed reasonable to suppose that this pressure increase was due to the increase in the number of gas particles in the tube, and so it was called ionization pressure. Experiments have been performed and reported[2] which show that this pressure increase is exactly proportional to the corona current, with the wire positive when dry air, hydrogen, nitrogen, carbon dioxide, oxygen and ammonia are the gases in the tube. Since the publication of this data Arnold[3] has contended that the pressure increase could be completely accounted for as the result of Joule's heat, and that the assumption that it is due to ionization is untenable. To support this contention Arnold performed experiments " by electrically heating the central wire in apparatus similar to Farwell's and " observed the pressure increase. With such an apparatus Arnold attempted to show (1) that an increase in pressure due to heat appears suddenly, (2) that for a given power consumed in the tube the increase in pressure due to heat is of about " the same magnitude as those observed " in the corona.

In order to show clearly that the pressure increase is not due to heat a series of comparative experiments were performed with the pressure increase caused, first, by producing the corona glow on the wire and, second, by heating the central wire. The pressure increase observed in the first set of experiments will be referred to as *caused by corona* and in the second set as *caused by heat.*

[1] Dr. S. P. Farwell, "The Corona Produced by Continuous Potentials," Proc. A. I. E. E. Nov., 1914. Dr. Jakob Kunz, "On the Initial Condition of the Corona Discharge," PHYS. REV., July, 1916.

[2] Earle H. Warner, "Determination of the Laws Relating Ionization Pressure to the Current in the Corona of Constant Potentials," PHYS. REV., Sept., 1916.

[3] H. D. Arnold, (Abstract) PHYS. REV., Jan., 1917.

A few computations have also been made which strengthen the results of the experiments.

II. EXPERIMENTAL RESULTS.

1. The reason why one who sees this pressure increase, as recorded by a quick-acting pressure meter, thinks it is not a heat effect, is because of rapidity with which it appears and disappears. Arnold showed that the pressure increase occurred quite rapidly when caused by heat. The following curves show the difference in the rapidity of appearance and disappearance of the pressure increase caused by heat, and caused by corona. It will be noticed in Fig. 1, where the pressure increase was caused by heating the central wire, that fifteen seconds was required for the prssure to come to its maximum value, and that from the time the current was broken twenty-five seconds was required for the pressure to return to practically its original value, while in Fig. 2, where the pressure increase was caused by corona, only three seconds was required for the maximum pressure to be attained and that the pressure came back to practically its original value in eighteen seconds. In this last case from the appearance of the phenomenon it seems, if the aneroid pressure meter had less inertia, that the pressure increase could be determined in less than three seconds. These curves show that the pressure increase appears five times as rapidly when caused by corona as when caused by heat, and disappears also more rapidly.

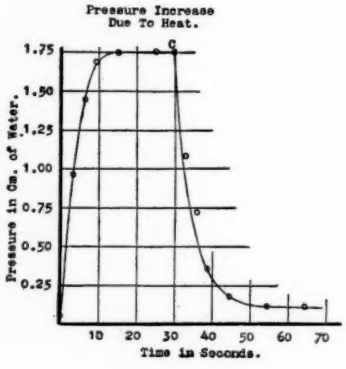

Fig. 1.

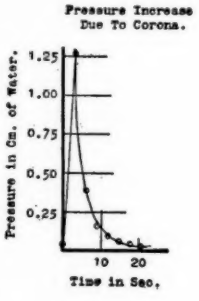

Fig. 2.

2. In the pressure increase due to corona, a short time interval of five to seven seconds occurs after the sudden increase of pressure, before the heat effect in the corona begins to be noticed. This is shown by an abrupt bend, A, in the curve where the pressure increase is plotted against time, as is done in Fig. 3. No such bend occurs in the case where the pressure increase is caused by heat alone, as is shown in Fig. 1. In the work which has previously been reported the pressure increase measurements were always taken at the point A, and this seems to be practically independent of the heat effect.

3. The heat which is produced in the corona discharge, shown by the gradual pressure increase from B to C, Fig. 3, is distributed throughout the whole volume of enclosed air and so, when the current is broken does not radiate rapidly because the air is a poor conductor. This is shown very clearly in Fig. 4. This seems to show that the pressure increase due to

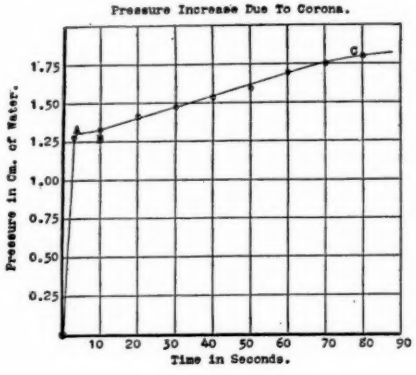

Fig. 3.

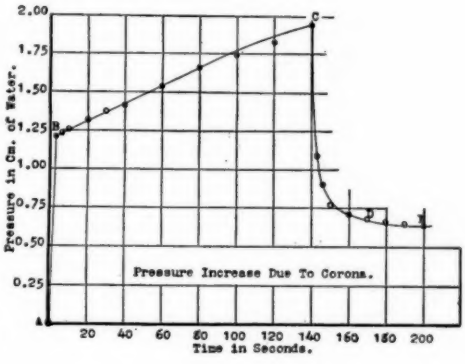

Fig. 4.

heat in the corona is represented by the difference of ordinates of C and B (Fig. 4). As soon as the corona current is broken at C the increase in pressure due to corona at once disappears, but the increase in pressure due to heat in the corona discharge remains, as is shown by the difference of ordinates of D and A. This difference is always very nearly equal to the difference of ordinates of C and B. This heat energy produced by the corona current, since it is distributed through the gas, radiates very slowly, as is shown by the gradual descent of the curve from D to E. No such effect is observed when the increase of pressure is due entirely to heat, as is shown in Fig. 1. This curve (Fig. 1) shows that twenty-five seconds after the current through the wire is broken at C the resultant pressure increase due to heat has practically disappeared; while Fig. 4 shows that twenty-five seconds after the corona is removed from the wire the increase in pressure due to the corona has disappeared, but practically all the pressure increase due to heat in the corona (ordinates C minus B approximately equals ordinates D minus A) still remains and radiates very slowly.

4. If the increase in pressure is due to heat, the same increase in pressure should result when the same power is consumed (*a*) with a corona current through the gas, (*b*) with a heating current through the wire. Figs. 5 and 6 show that this is not the case. The powers consumed in the two cases are not exactly the same, but one can see that were they the same, the increase in pressure due to corona would be approxi-

mately one half the increase in pressure due to heat. The power in the case of the corona was obtained by multiplying the potential difference between the wire and the tube by the corona current, and in the case of

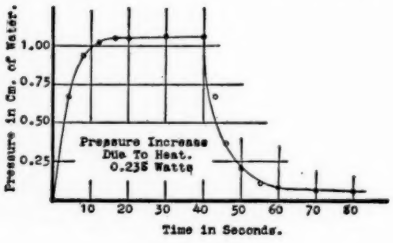

Fig. 5.

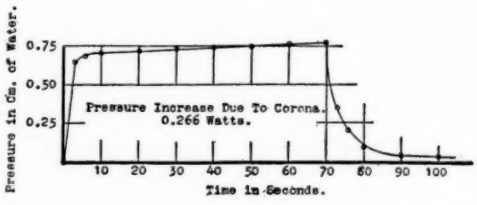

Fig. 6.

the heated wire was obtained by multiplying the current through the wire by the potential difference across that portion of the wire which was in the tube.

5. If the increase in pressure in the corona discharge is due to heat the temperature of the air in the corona tube must increase. This may or may not be the case in the luminous layer near the wire but the temperature of the gas in the tube at a point four millimeters from the wire actually decreases. This was determined by inserting a sensitive thermocouple made of very fine Copper-Advance wire into the corona tube. The temperature decreased only at the instant the corona appeared. In a short time, after the heat due to the corona began to appear (corresponding to the slope B to C, Figs. 3 and 4) the temperature of the gas in the tube began to increase. This cooling effect is shown in Fig. 7. Comparing Figs. 7 and 3 it is seen that the increase in pressure which was measured at A was observed while there was an actual cooling in the corona tube. This cooling should be expected when air or oxygen are in the tube, for under these conditions ozone is formed. Since the formation of ozone from oxygen is always accompanied with an absorption of heat the temperature of the air or oxygen would tend to lower. Mr. J. W. Davis, working on corona about hot wires in hydrogen, has discovered that the appearance of the corona about a tungsten wire heated to white heat, causes it to cool to dull red. This tends to show that even in the corona glow itself there is a cooling effect.

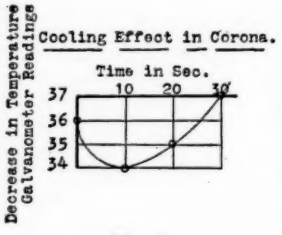

Fig. 7.

6. If the increase in pressure in the corona is due to heat one should expect it to be the same with the wire either positive or negative. As has been previously mentioned it is impossible to obtain measurements

when the wire is negative because of the presence of beads. The negative corona is entirely different from the positive corona.

7. The following consideration will further show that the increase in pressure can not be due to heat. The heat produced by the corona current will be given by the equation $H = 0.238\ eit$ and, if the observed pressure increase is due to heat, the increase in pressure Δp will be proportional to the heat, and we can write $\Delta p = k\ eit$. Now the only way for Δp to vary directly as i, the corona current, as is the case—shown by curves in the last article—is for e to be independent of i. Data shows that this is not the case.

III. Results from Theoretical Considerations.

1. If the increase in pressure is due to heat it is possible to compute the magnitude of the pressure increase when one knows the watts of electrical energy consumed in the tube. The trial represented in Fig. 6 gives us this data. The observed pressure increase was measured in three seconds so that the total number of joules of work consumed by the tube in that time was $3 \times 0.266 = 0.798$ joules and this corresponds to 0.1909 calories. Knowing the volume of the tube, the temperature and pressure of the air in it, the mass of the air in the tube can be computed. With the above-mentioned quantity of heat and mass of air, together with the specific heat of the air at constant volume, the temperature rise of the air can be computed, assuming that the electrical energy is converted into heat. This temperature rise comes out to be 2.44° C., which at constant volume corresponds to a pressure increase of about nine cm. of water, while the observed pressure increase in this particular trial amounts to about seven tenths cm. of water. In this computation radiation and conduction losses have been neglected because they would be very small from a body 2.44° C. above room temperature. This shows that the observed results lie in a different order of magnitude from what would be expected if Arnold's theory were true.

2. Arnold states, if "we compute the corona currents that would result from the presence of enough ionized particles to produce the observed pressure changes, the currents calculated are many thousand times greater than those actually obtained." Such a statement is only true when the ionized particles are produced in a uniform or practically uniform electric field. This is not the case in the corona tube. H. T. Booth is publishing data on the distortion of the field in the corona tube. This data shows that the potential gradient near the wire is very high—of the order of 30,000 volts per cm. This is the arcing gradient, in which it is probable every molecule is ionized. Then for a long space between the

wire and the tube there is a very small gradient. With this condition of the field, near the wire every molecule may be ionized and still the resultant current be very small, for few of the ionized particles near the wire will pass through the space where there is a small gradient. Simple computations based on kinetic theory show that the maximum observed pressure increases can be explained by ionization if every molecule of the air within 1.39 mm. of the wire is ionized. Within this distance the potential gradient is equal to the arcing gradient and therefore probable that all molecules are ionized.

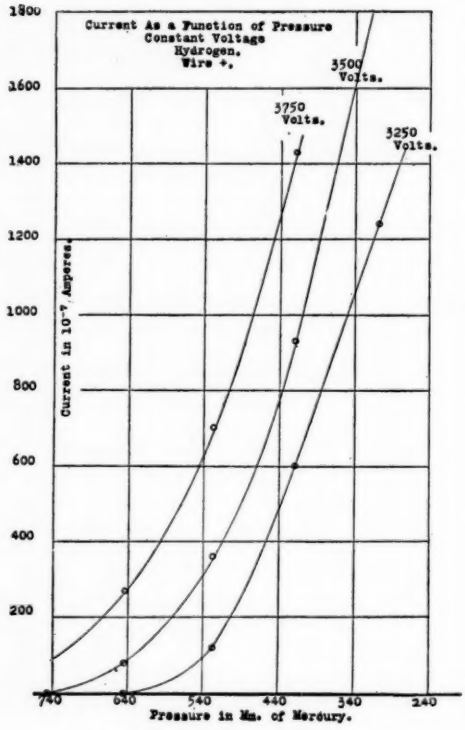

Fig. 8.

IV. Further Verification of Kunz's Theory.

The final equation as presented in the last article is

$$ki = \frac{v_0}{e}(p_1 - p_0) + \text{a constant},$$

where i is the corona current, v_0 the volume of the tube, e the potential difference between the wire and the tube, $p_1 - p_0$ the pressure increase, k a constant and p_0 the initial pressure. This equation shows that for a constant potential difference e, the current i should increase as p_0 is lowered. Data were taken, by measuring the current at various measured pressures, caused by a constant potential difference, which verifies this theory. These data are shown graphically in Figs. 8 and 9 when pure hydrogen and nitrogen respectively were the gases in the tube.

V. Summary and Conclusions.

Experimental results show:

1. That the increase in pressure due to corona appears and disappears much more rapidly than when due simply to heat.

2. That the heat in the corona discharge is not a prominent factor until many seconds after the corona appears.

3. That in equal energy experiments the increase in pressure due to corona differs from the increase in pressure due to heat by about 50 per cent.

4. That at the instant the corona appears the gas in the tube at a small distance from the wire is cooled.

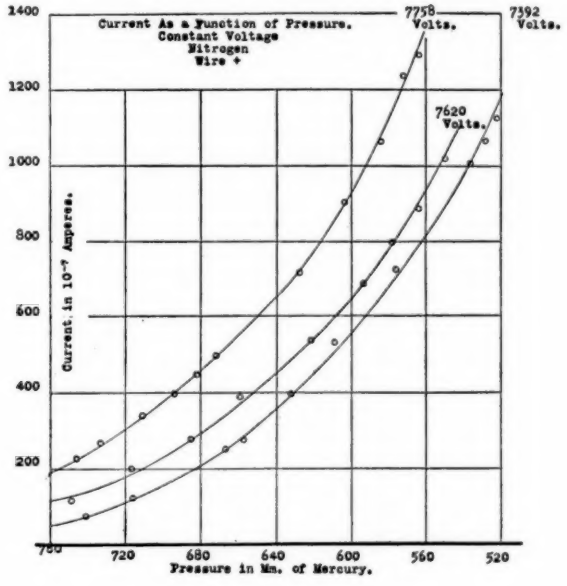

Fig. 9.

5. That the theory advanced by Kunz is verified in one more field, namely in the relation between current and pressure for constant voltage.

These results together with conclusions drawn from simple calculations, force one to believe that the pressure increase in the corona discharge is not due to Joule's heat. With the recent knowledge of the distortion of the field in the corona tube it seems very possible that the increase in pressure is due to ionization.

The writer desires to express his appreciation to Professor A. P. Carman for the use of the laboratory facilities, and to Dr. Jakob Kunz for his continued interest and suggestions.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
June, 1917.

THE EMISSION OF ELECTRONS IN THE SELECTIVE AND NORMAL PHOTO-ELECTRIC EFFECTS.

BY A. LL. HUGHES.

THE selective and normal photo-electric effects have been investigated almost entirely through a study of the variation in the total number of electrons emitted from suitable metallic surfaces, with the wave-length of the light used. It is therefore desirable to attack the problem in another way in the hope that some evidence as to the difference between the two effects may be obtained. The author[1] attempted this in an investigation of the distribution of electrons emitted from a surface of sodium-potassium alloy. The results showed that the distribution was not identical for the selective and for the normal photo-electrons, but did not settle whether the difference was one in the *direction-distribution* or in the *velocity-distribution* of the photo-electrons in the two effects. The following experiments show that there is a definite difference in the direction-distribution of the photo-electrons.

The apparatus consisted of a glass tube about 5 cm. wide, provided with three aluminum electrodes as shown. These could be connected to an electrometer separately or together. Two small apertures, at opposite sides of the cylindrical electrode C allowed a narrow beam of light to pass in and out. The light was focused on to a small area (about 4 mm. square) at the center of the sodium-potassium alloy surface. A mercury lamp was used as source of light. To secure light of the wave-length corresponding to the maximum of the selective photo-electric effect, it was passed through a Wratten blue filter (made by the Eastman Company) to isolate the blue lines of the mercury arc. The ratios of the solid angles subtended at the center of the surface of the alloy, by the electrode A, by $A + B$, and by $A + B + C$, were roughly as 15:55:100. The tube was exhausted by the charcoal liquid air method and sealed off.

The method of experiment was to measure the number of electrons received by A, by $A + B$, and by $A + B + C$ respectively, when there was no field to make the electrons deviate from their straight line paths. It is not sufficient to connect the alloy and the electrodes to earth to secure the absence of an electric field, the contact difference of potential must be annulled. A very convenient way of doing this was suggested

[1] Hughes, Phil. Mag., XXXI., p. 100. Feb., 1916.

by the work of Millikan.[1] Let V be the negative potential which is necessary to apply to $A + B + C$ in order to stop the fastest electrons emitted from the alloy when illuminated by (unpolarized) light of frequency ν. Then $V + K$ is the total potential difference between the electrodes $A + B + C$ and the alloy where K is the contact difference of potential. Let ν_0 be the lowest frequency capable of causing the emission of photo-electrons from the alloy. Then we have

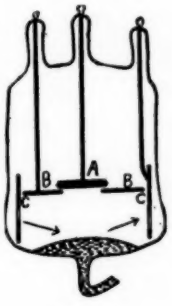

Fig. 1.

$$e(V + K) = h\nu - h\nu_0,$$

$$K = \frac{h}{e}(\nu - \nu_0) - V.$$

To get the lowest frequency capable of exciting the photo-electric effect, a powerful carbon arc was used to illuminate the surface in conjunction with several red and orange filters. A barely measurable effect was obtained when the light was filtered through a thin molybdenite flake which was opaque to light of wave-length shorter than λ 7,100. This was therefore taken as the long wave-length limit of the photo-electric effect of the sodium-potassium alloy. A potential of .35 volt was sufficient to stop the electrons due to the green line (λ 5,461) of the mercury arc. Applying this to the above formula, we get $K = .31$ volt. This is probably subject to an error of $\pm .05$ volt, on account of some uncertainty in the determination of the long wave-length limit. (It should be observed that this value of the contact difference of potential between the sodium-alloy and the aluminum electrodes is smaller than might have been expected.) Thus to secure the absence of an electric field between the alloy and the electrodes A, B, and C, the alloy must be made .3 volt negative with respect to them.

On illuminating the alloy with light polarized successively in the $E\|$ and in the $E\perp$ planes (that is, with the electric force parallel and perpendicular to the plane of incidence respectively), the ratio of the selective to the normal effect foi the electrons caught by A, by $A + B$, and by $A + B + C$ in turn were found to be as follows:

Collecting Electrodes	Ratio $\frac{\text{selective effect}}{\text{normal effect}}\left(\frac{E\|\|}{E\perp}\right)$
$A + B + C$	10.3
$A + B$	11.7
A	17.5

These observations indicate a greater concentration of the selective

[1] Millikan, PHYS. REV., VII., p. 18, Jan., 1916.

photo-electrons along directions near the perpendicular to the surface, as compared with the normal photo-electrons. In the normal effect the charges received by A, $A + B$, $A + B + C$, were as 16:60:100 while in the selective effect they were as 27:81:100. The normal photo-electric distribution is therefore closer to that which would be obtained on the supposition that equal numbers of electrons are emitted per unit solid angle, regardless of direction (15:55:100). No attempt was made to allow for reflection of electrons in this rough comparison. To make sure that those results might not be due in some way to the field not being zero, on account of an error in estimating the contact difference of potential, the observations were repeated twenty-four hours later with different negative potentials applied to the alloy.

Collecting Electrode.	Ratio $\frac{\text{selective effect}}{\text{normal effect}}\left(\frac{E1}{E1}\right)$. Potential on the Alloy.		
	−.5 Volt.	−.3 Volt.	−.1 Volt.
$A+B+C$	9.6	10.2	10.1
$A+B$	11.1	11.5	10.7
A	13.3	13.8	14.8

These results show that slight departures from exact compensation of the contact difference of potential do not affect the ratios to any great extent. We may therefore conclude that the ratios really indicate a difference in the direction distribution of the photo-electrons in the selective and normal photo-electric effects. That the selective photo-electrons tend to crowd more along the perpendicular to the surface than the normal photo-electrons might, at first sight, be expected, since the electric force in the light has a component along the perpendicular to the surface. Calculation shows however that it is impossible for an electron vibrating about a position of equilibrium, to acquire energy of the order of that possessed by a photo-electron, from the electric force in the light beam, unless we suppose that the vibration is undamped and that the electron can go on accumulating energy undisturbed, for over a million vibrations. One then turns to the view that there are vibrating systems, which, over a certain range of frequency, are more easily broken up by alternating electric forces (of the right frequency) perpendicular to the surface, than by electric forces parallel to the surface.

The presence of a maximum on the curve connecting the number of electrons emitted per unit energy of the incident light, with the wave-length, has been taken to mean that the selective photo-electric effect is a resonance phenomenon. As Pohl and Pringsheim[1] have shown in the

[1] Pohl and Pringsheim, Verh. d. Deutsch. Phys. Ges., XV., p. 111, 1913.

case of one metal at least, the mere presence of a maximum may be completely accounted for by a consideration of the depth to which the light penetrates into the surface and the chances which the photo-electrons produced at different depths have of emerging. When the conditions are arranged so that the light is absorbed in a very thin layer (that is, by using a very oblique beam), so that all the photo-electrons released in the surface have a greater chance of emerging, then the maximum disappears. The real selective photo-electric effect as defined by Pohl and Pringsheim, however, needs more than a maximum on the curve to indicate its presence; the photo-electric effect associated with light polarized in the $E\|$ plane must be several times larger than that associated with light polarized in the $E \perp$ plane, and also must possess a pronounced maximum at some wave-length in the region where the maximum appears. Indeed, the maximum appears only in the photo-electric effect produced by light polarized in the $E\|$ plane. Moreover this maximum must become more and more pronounced as the obliquity is increased, that is, as the electric force in the light beam becomes more and more perpendicular to the surface. Either the light polarized in the $E\|$ plane is absorbed in a very much smaller depth than the light polarized in the $E \perp$ plane, with the result that the photo-electrons produced by light polarized in the $E\|$ plane escape from the surface in greater numbers; or else there must be resonance systems in the surface which have the property of responding only when the electric force in the light beam has a component perpendicular to the surface. There is no evidence from optics to support the first hypothesis. So far as the maximum emission velocity is concerned, the work of Richardson and Compton[1] and of Millikan[2] shows that there is nothing unusual in the behavior of the photo-electrons from sodium, even in the region where the maximum selective effect is observed, when compared with other metals which give only the normal effect. Hence on the second hypothesis, it would be necessary to suppose that the special systems which give rise to the selective effect are fundamentally of the same nature as those which give rise to the normal effect. The selective effect would then be due to the fact that there is an exceptionally large number of systems of a certain period so oriented as to respond to light polarized so that there is an electric force perpendicular to the surface.

The results obtained in this paper suggest a systematic examination of the velocity distribution and the direction distribution of photo-electrons

[1] Richardson & Compton, Phil. Mag., XXIV., p. 575, 1912.

[2] Millikan, PHYS. REV., VII., p. 355, March, 1916. Millikan and Souder, Proc. Nat. Acad. of Sci., II., p. 19, Jan., 1916.

emitted from surfaces illuminated by polarized light. It is proposed to carry out the experiments on metals which show the selective effect such as sodium-potassium alloy and on metals such as mercury which show only the normal effect. By using liquid surfaces, we can be much more certain that the plane of polarization of the light has a definite meaning with respect to the plane of the surface.

These experiments were carried out in the Palmer Physical Laboratory at Princeton during the summer of 1916. I wish to express my best thanks to Professor Magie for placing the facilities of the laboratory at my disposal.

THE RICE INSTITUTE,
HOUSTON, TEX.

THE IONIZING POTENTIALS OF GASES.

BY A. LL. HUGHES AND A. A. DIXON.

INVESTIGATIONS on the least energy required to ionize molecules of a gas by the impact of electrons lead to results which may often be used to test theories of atomic structure. Such experiments are better known as experiments on the ionizing potentials of gases. Of the recent experiments on this subject, the best known are those of Franck and Hertz.[1] During the past year, the results of some of these experiments have been verified and extended by Goucher[2] and Bazzoni.[3] Yet up to the present, the ionizing potentials of only six or seven gases are known. It was thought that a systematic investigation of the ionizing potentials of a number of gases—compounds as well as elements—would prove valuable. It was also thought worth while to measure the ionizing potentials of some gases which have already been investigated to see whether the modifications in the experimental methods lead to appreciable changes in the published constants.

FIRST METHOD.

In the method used by Franck and Hertz and by Goucher, the electrons are accelerated by an electric field up to a gauze, and a certain proportion of them pass through the interstices into another region where they are subjected to a retarding field. The positive ions produced in this region are driven into an electrode connected with an electrometer. One obvious defect of this method is that, at potentials just above the ionizing potentials, the part of the gas in which ions can be produced is limited to a thin layer close to the gauze, for the electrons are quickly retarded to a speed below which they do not ionize. A method in which all the gas can be ionized, even when the applied potentials are close to the ionizing potentials offers advantages in precision in fixing the ionizing potentials. The apparatus shown in Fig. 1 approximately satisfies this condition. The photo-electrons from a platinum disc P, illuminated by ultra-violet light, were accelerated by a suitable electric field towards the hollow platinum cylinder C. To prevent any spreading out of the electron stream, a solenoid carrying a current was arranged coaxial with the tube. The

[1] Franck and Hertz, Verh. d. Deutsch. Phys. Ges., XV., p. 34, 1913.
[2] Goucher, PHYS. REV., VIII., p. 561, Nov., 1916.
[3] Bazzoni, Phil. Mag., XXXII., p. 566, Dec., 1916.

electrons would be compelled to travel in narrow spirals along the lines of magnetic force, and so to keep to the center of the tube. A small field of a volt or two inside the cylinder was sufficient to drive the positive ions produced to the electrode D (a strip of platinum about three mm. wide). The advantage of this form of apparatus was that, once the electrons had passed into the cylinder, their velocity would hardly be affected by the small field inside the cylinder, and consequently they would be available for ionization almost all along their path, in contrast with the conditions obtained with the Franck and Hertz type of apparatus. The curves in Fig. 2 show the way in which the ionization inside the cylinder varies with the potential difference accelerating the electrons from the disc to the cylinder. One curve was obtained with the Gaede mercury pump running continuously, so that the residual gas was mercury vapor at a pressure of about .002 mm. The second curve —showing less ionization—was obtained with air also in the apparatus at a pressure of .0026 mm. The intersection of these curves with the axis takes place at about 9.45 volts. We must, however, take into account the fact that the photo-electrons are emitted with a small velocity from the disc. How much to allow for this velocity of emission is rather difficult to say. Since the line λ 2,537 is by far the strongest line in the ultra-violet spectrum of the mercury arc, we have taken this to be, for our purpose, the shortest line emitted by the mercury lamp. From Richardson's and Compton's curves[1] on the distribution of velocities among the photo-electrons, it is evident that most of the electrons excited by the shorter lines have velocities less than those of the *fastest* electrons produced by λ 2,537. We therefore consider it justifiable to neglect the light of shorter wave-length than λ 2,537. From Richardson and Compton's experiments we know that the long wave-length limit of the photo-electric effect for platinum is λ 2,910. By means of the equation

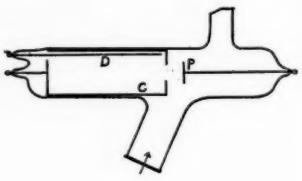

Fig. 1.

$$Ve = h\nu - h\nu_0$$

we can get the velocity (measured in equivalent volts) of the fastest electrons due to λ 2,537. Taking $h/e = 4.13 \times 10^{-15}$ (volt-frequency units, Millikan) and

$$\nu = \frac{3 \times 10^{10}}{2537 \times 10^{-8}}, \quad \nu_0 = \frac{3 \times 10^{10}}{2910 \times 10^{-8}},$$

we get $V = .63$ volt. Adding this to the accelerating potential 9.45 volts,

[1] Richardson and Compton, Phil. Mag., XXIV., p. 577, 1912.

we get 10.08 volts, or to the nearest tenth of a volt, 10.1 volts, as the ionizing potential of mercury vapor. (We may note that the straight part of the curve intersects the axis at 10.15 volts. This could be associated with the electrons emerging with practically no initial velocity, though it can be shown that this agreement could only be expected as an approximation.)

To find the ionizing potentials of other gases, the mercury vapor was frozen out of the experimental tube by surrounding a U-tube between the experimental tube and the pump with carbon dioxide snow. It can readily be shown, and verified by experiment, that there is a certain pressure at which the ionization is a maximum, for if the pressure be too low, there will be few molecules available for ionization, and if the pressure be too high, the electrons will be used up before they enter the cylinder.

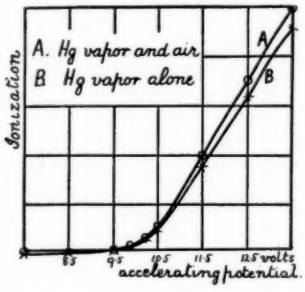

Fig. 2.

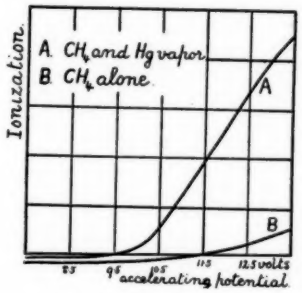

Fig. 3.

On carrying out the experiments, using hydrogen, oxygen, and methane in turn, and choosing the most favorable pressure, it was found that the ionization was surprisingly small in comparison with that in mercury vapor. When investigating the ionizing potential in mercury vapor, a small negative current was obtained for accelerating potentials below the ionizing potential. This did not cause any inconvenience, as the ionization curves were so steep. Fig. 3 shows that the inclination of the ionization curve for methane (the hydrogen and oxygen curves were much the same) was much less than for mercury vapor, and moreover, the negative part of the curve is greater in the absence of mercury vapor. The negative part could not be reduced appreciably either by increasing the magnetic field or by increasing the electric field inside the cylinder. This made it impossible to determine the ionizing potential for gases other than mercury vapor with any accuracy, as there was no definite discontinuity in the curves. The method was therefore of little use, in spite of its attractive features, except for the determination of the ionizing potential of mercury vapor. It served to show that the ioniza-

tion of mercury vapor by electrons with energy exceeding 10.1 volts is much more intense than that of other gases even when the most favorable pressures are selected. No evidence for ionization by electrons with energies between 4.9 volts and 10 volts was obtained; had the electron current been more intense, it would probably have been observed.

No satisfactory explanation of the negative part of the curves can be given. It was not due to light getting into the cylinder. Some electrons might possibly stick to molecules and become negative ions travelling with the ordinary molecular velocities. For such velocities, however, the electric field inside the cylinder should be ample to prevent any negative ions from reaching the electrode. The electrons may rebound with their full velocities from molecules. Even so, the magnetic field should be sufficient to prevent them reaching the electrode *D*. If this were the explanation, it would suggest that the collisions with the mercury molecules were non-elastic, while those with the other molecules were elastic, a result not in agreement with Franck and Hertz's experiments.

SECOND METHOD.

The method which was finally adopted for the measurement of ionizing potentials was the same in principle as that of Franck and Hertz. A diagram of the apparatus is shown in Fig. 4. It was made entirely of glass and platinum, the amount of metal used being reduced to a minimum. Between what may be called the " experimental tube " and the pump on the one hand and the supply bulb stopcock on the other, traps were provided by which any vapor could be frozen out by liquid air or some other cooling agent. The electrons were emitted from a filament *F*, about two or three mm. away from the disc *D*, which was provided with a narrow slit 2 mm. × .5 mm. across the direction of the filament. These electrons were accelerated by an electric field between the filament and the disc. About 5 mm. beyond the disc was an electrode *E*. To get an ionization curve, *E* was connected to an electrometer (sensitivity about 1,000 divisions per volt) and the filament *F* to a positive potential of 3 volts. This prevented any electrons emitted by the filament *F* from reaching the electrode *E*. The potential (positive) of *D* was varied so as to increase the accelerating potential step by step, and the positive charge acquired by *E* was measured against the accelerating potential. To get a velocity distribution curve, the difference of potential between *F* and *D*

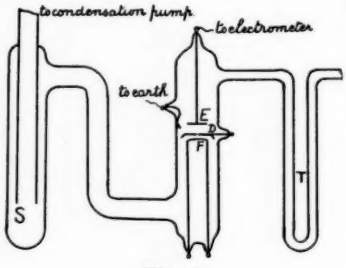

Fig. 4.

was maintained at some suitable value, and the negative charge acquired by E was measured for different retarding potentials between D and E. Fig. 8 is a typical velocity distribution curve. It shows that the " 7.46 volt " electrons (electrons produced by an accelerating field of 7.46 volts) have velocities corresponding to values between 10.0 volts and 11.5 volts. (Strictly speaking, the real energy distribution curve, and from it the real velocity distribution curve, is given on differentiating the experimental curve in Fig. 8. As all the information we require can be obtained at a glance from the experimental curves, it was thought unnecessary to differentiate each curve.) When we used apparatus made of glass and brass joined together with sealing wax, the velocity distribution curves were generally very unlike those shown in this paper. The curves seemed to indicate that electrons of all velocities from zero up to a maximum (often considerably less than that corresponding to the applied potential) were present. This may be attributed to the formation of polarization layers on the metal surfaces which have the property of modifying the field in the apparatus very considerably. The state of these polarization layers very probably changes rapidly on passing through an aperture from one side of a plate which receives many electrons to the other side which receives none. There will therefore be strong electric fields in the neighborhood of the aperture which may change the velocity and the direction of motion of the electrons passing through the aperture. This experience leads us to doubt conclusions

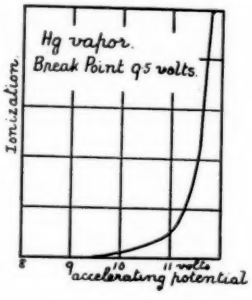

Fig. 5.

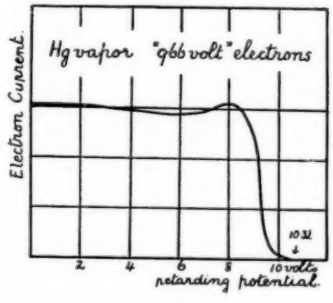

Fig. 6.

drawn from experiments in which slow moving electrons are involved, when the experimental apparatus contains brass or such metals joined to glass by sealing wax and with tap grease in close proximity to the place where the electrons are impinging on surfaces. Velocity distribution curves should be taken, as it is unlikely that the actual velocity of the electrons really corresponds to the applied potential. Indeed, with our apparatus, designed to reduce surface polarization effects as much as

possible, we had distinct evidence that with some gases slight surface films were formed.

When working with gases at a pressure of about .01 mm. of mercury, it is difficult to be sure that the gas remains pure, especially if there is a glowing filament in the apparatus. We therefore used the constant flow method of supplying the gas. A supply bulb, of a liter capacity,

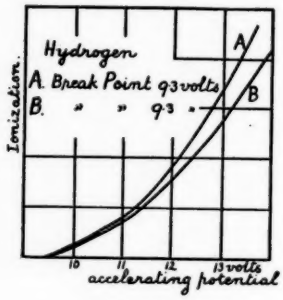

Fig. 7.

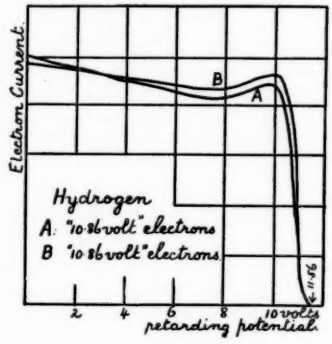

Fig. 8.

was filled with gas prepared from pure chemicals and purified according to the usual methods. Between this bulb and the experimental tube was a very fine capillary tube, through which the gas flowed slowly. The gas was removed from the apparatus by a Langmuir condensation pump. By adjusting the pressure in the supply bulb, which determined the rate of flow through the capillary tube, the pressure in the experimental tube could be maintained at any value below .1 mm. Vapors were prevented from entering the experimental tube by cooling the traps T and S on each side of it by liquid air. In some cases, in which liquid air would reduce the pressure of the gas under observation to practically zero, carbon dioxide snow was used.

The pressure of the gas gradually diminished during the course of a set of observations owing to a decrease in the amount of gas in the supply bulb. The pressures at the beginning and at the end of a set of observations are indicated for each gas. To save space, the ionization curves and the corresponding velocity distribution curves are shown for four gases only. They are chosen so as to illustrate the greatest variation in the shapes of the curves. These will be taken as types and the curves for the other gases will be indicated by reference to one or other of these four types.

An uncoated platinum filament was used to supply the electron current in the experiments on the first gases worked with, viz., ethylene, methane, ethane and carbon dioxide. A lime-coated filament was used in all the

succeeding experiments. The electron currents were unusually small in the gases carbon dioxide, oxygen, hydrochloric acid, chlorine and bromine, and the filament had to be heated almost to its melting point. On account of their chemical activity, the experiments on bromine and chlorine were troublesome to carry out and consequently only one set of observations was made for each of these gases.

The Results.

Mercury Vapor.—The ionizing potential of mercury vapor was found by running the condensation pump until the pressure was below .00001 mm. (the limit of the gauge). As the traps were not cooled by liquid air, the only gas present in appreciable quantity was mercury vapor. The ionization curve for mercury vapor is shown in Fig. 5. The curve starts from the axis at 9.5 volts; we shall refer to this point as the "break point." The velocity distribution curve obtained in mercury vapor is shown in Fig. 6. The actual accelerating potential for the electrons was 9.66 volts, the velocity distribution curve shows that the fastest of them

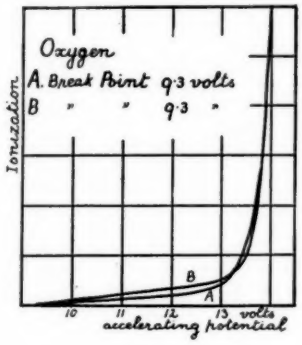

Fig. 9.

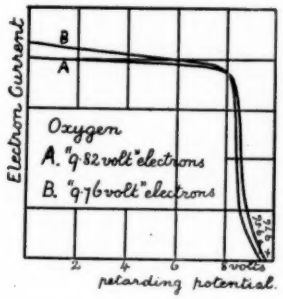

Fig. 10.

had a velocity corresponding to 10.35 volts. We therefore correct the applied potentials in the ionization curves by adding 10.35 − 9.66 volts to the value 9.5 volts which gives 10.19 volts as the ionizing potential for mercury vapor. No evidence of ionization in mercury vapor by electrons with velocities corresponding to 4.9 volts, or to any potential between this and 10.2 volts, was obtained. The pressure of the mercury vapor was not specially adjusted so as to give the maximum amount of ionization. If ionization is produced by electrons with velocities below 10.2 volts, it is clear that it is of a different order from that produced by electrons with velocities greater than this value. We believe, however, that the explanation given by Bohr[1] and by Van der Bijl,[2] that the ioniz-

[1] Bohr, Phil. Mag., XXX., p. 410, Sept., 1915.

[2] Van der Bijl, Phys. Rev., IX., p. 173, Feb., 1917.

ation produced by electrons whose velocities are below 10.2 volts is a secondary effect, and does not represent real ionization by impact, is probably correct.

Hydrogen.—Hydrogen was prepared by the action of pure caustic potash on pure aluminum. It was passed through a tube of red hot copper gauze to remove traces of oxygen and then through a spiral immersed in liquid air. The supply bulb was filled several times with hydrogen so prepared and pumped out completely between each filling.

It will be noticed that the ionization curve in hydrogen differs somewhat from that in mercury vapor. The velocity distribution curve *A*

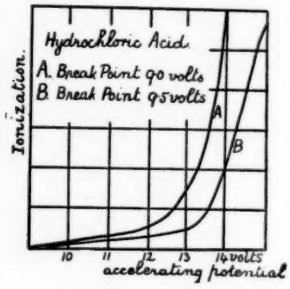

Fig. 11.

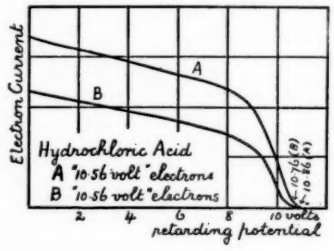

Fig. 12.

was obtained immediately after the ionization curve *A* and the former was used to deduce the correction to the ionizing potential as obtained from the latter. The pressures given are those obtained at the beginning and at the end of the set of observations.

A. Pressure .0303 − .0176 mm.
Break point 9.5 volts.
Correction from the velocity distribution curve, 11.56 − 10.86 volts.
Ionizing potential 9.5 + .7 = 10.2 volts.

B. Pressure .0152 − .0137 mm.
Break point 9.5 volts.
Correction from the velocity distribution curve, 11.56 − 10.86 volts.
Ionizing potential 9.5 + .7 = 10.2 volts.

To test whether the ionization curve was really due to hydrogen, the flow of gas was stopped, and in a short while the pressure was down to .00001 mm. At the same time, the ionization current for 14.46 volts accelerating potential was reduced from 101 to 5, showing that the ionization curves were almost entirely due to hydrogen.

Oxygen.—Oxygen was prepared by the action of water on "Oxone" cartridges. The oxygen was said to be 99.4 per cent. pure. It was passed through a soda lime tube to dry it. Several liters were prepared

and condensed in a tube surrounded by liquid air. About one third of this was allowed to boil away, the next third was used to wash out the supply bulb and finally to fill it, and the last third was rejected. There is reason to believe that the oxygen actually used in the experiment was very pure. The ionization curve for oxygen rises slowly from the axis for several volts and then very quickly, as though the gas is much more easily ionized by electrons whose velocity is a few volts above the ionizing potential. Owing to the small electron currents and the correspondingly small ionization currents, it was difficult to decide exactly where to place the break point.

A. Pressure .0176 − .0160 mm.
Break point 9.3 volts.
Correction from the velocity distribution curve 9.76 − 9.82 volts.
Ionizing potential 9.3 − .06 = 9.24 volts.

B. Pressure .0116 − .0102 mm.
Break point 9.3 volts.
Correction from the velocity distribution curve 9.56 − 9.76 volts.
Ionizing potential 9.3 − .20 = 9.10 volts.

Hydrochloric Acid.—Hydrochloric acid gas was prepared by dropping sulphuric acid on pure sodium chloride. The gas was condensed by liquid air, and allowed to evaporate, the middle portion being taken to wash out the supply bulb and to fill it with the gas to be tested. The electron current from the filament was much smaller than usual. The shape of the velocity distribution curve indicated that electrons of all velocities were present or else that some electrical distribution around the edge of the hole caused the electrons to deviate from their straight line paths to a considerable extent. Such a state of affairs might possibly be brought about by a small polarization layer on the surface of the electrode *D*. The ionization curve is similar to that of oxygen.

A. Pressure .0116 − .0116 mm.
Break points 9.0 volts.
Correction from the velocity distribution curve 10.86 − 10.56 volts.
Ionizing potential 9.0 + .30 = 9.30 volts.

B. Pressure .0221 − .0212 mm.
Break point 9.50 volts.
Correction from the velocity distribution curve 10.76 − 10.56 volts.
Ionizing potential 9.50 + .20 = 9.70 volts.

Carbon Monoxide.—Carbon monoxide was prepared from formic acid and concentrated sulphuric acid. The gas passed through caustic potash

solution and then through a spiral immersed in liquid air. The supply bulb was filled and pumped out several times before the final filling.

Ionization curve: hydrogen type.

Velocity distribution curve: hydrochloric acid type.

A. Pressure .0212 − .0185 mm.
Break point 7.45 volts.
Correction from the velocity distribution curve, 7.10 − 7.52 volts.
Ionizing potential 7.45 − .42 = 7.03 volts.

B. Pressure .0144 − .0130 mm.
Break point 7.45 volts.
Correction from the velocity distribution curve, 7.10 − 7.46 volts.
Ionizing potential 7.45 − .36 = 7.09 volts.

C. Pressure .0116 − .0109 mm.
Break point 7.50 volts.
Correction from the velocity distribution curve, 7.32 − 7.42 volts.
Ionizing potential 7.50 − .10 = 7.40 volts.

Carbon Dioxide.—Carbon dioxide was prepared by heating sodium bicarbonate. The gas was passed through concentrated sulphuric acid and then solidified in a tube surrounded by liquid air. This was then allowed to evaporate, the middle portion being used to wash out the apparatus and to fill the supply bulb. Fractionating a gas from the solid state instead of from the liquid state is probably less satisfactory as a means of purification. The vapor traps in these experiments were cooled by a mixture at − 90° C. instead of by liquid air.

Ionization curve: hydrogen type.

Velocity distribution curve: oxygen type.

A. Pressure .0137 − .0123 mm.
Break point 9.85 volts.
Correction from the velocity distribution curve, 10.2 − 10.0 volts.
Ionizing potential 9.85 + .20 = 10.05 volts.

B. Pressure .0168 − .0168 mm.
Break point 9.70 volts.
Correction from the velocity distribution curve, 10.20 − 10.00 volts.
Ionizing potential 9.7 + .2 = 9.9 volts.

Nitrogen.—Nitrogen was prepared by heating sodium nitrite and ammonium chloride with a little distilled water. The gas was passed through concentrated sulphuric acid and through a tube containing red hot copper gauze. Several liters of gas were generated and used to wash out the apparatus before the final filling of the supply bulb was made.

Ionization curve: mercury vapor type.

Velocity distribution curve: oxygen type.

A. Pressure .0123 − .0116 mm.
Break point 7.45 volts.
Correction from the velocity distribution curve 7.72 − 7.52 volts.
Ionizing potential 7.45 + .20 = 7.65 volts.

B. Pressure .0102 − .0096 mm.
Break point 7.8 volts.
Correction from the velocity distribution curve 7.52 − 7.52 volts.
Ionizing potential 7.8 + 0 = 7.80 volts.

C. Pressure .0250 − .0221 mm.
Break point 7.9 volts.
Correction from the velocity distribution curve 7.32 − 7.52 volts.
Ionizing potential 7.9 − .2 = 7.70 volts.

Hydrogen Sulphide.—Hydrogen sulphide was prepared by the action of dilute sulphuric acid on ferrous sulphate. The gas was washed through dilute sulphuric acid and then frozen by liquid air. This was allowed to liquefy and then to evaporate, the middle portion being used to wash out the apparatus and to fill the supply bulb with the gas for the experiment. As this gas liquefies easily, the traps were surrounded by a mixture at about −70° C.

Ionization curve: mercury vapor type.
Velocity distribution curve: hydrochloric acid type.

A. Pressure .0160 − .0152 mm.
Break point 9.2 volts.
Correction from the velocity distribution curve 10.40 − 10.16 volts.
Ionizing potential 9.20 + .24 = 9.44 volts.

B. Pressure .0123 − .0116 mm.

C. Pressure .0109 − .0102 mm.

D. Pressure ? − .0032 mm.

Break point for *B*, *C*, and *D* 8.5 volts.
Correction from the velocity distribution curves, 10.76 − 10.16 volts.
Ionizing potential 8.5 + .6 = 9.1 volts.

Nitric Oxide.—Nitric oxide was prepared by the action of nitric acid on pure copper. The gas was passed through distilled water and caustic soda. It was then liquefied and as usual the middle fraction of the evaporating liquid was passed into the supply bulb.

Ionization curve: mercury vapor type.
Velocity distribution curve: hydrogen type.

A. Pressure .0176 − .0152 mm.
Break point 8.9 volts.
Correction from the velocity distribution curve, 10.10 − 9.62 volts.
Ionizing potential 8.9 + .48 = 9.38 volts.

B. Pressure .0130 − .0123 mm.
Break point 8.8 volts.
Correction from the velocity distribution curve, 10.10 − 9.56 volts.
Ionizing potential 8.8 + .54 = 9.34 volts.

C. Pressure .0109 − .0103 mm.
Break point 8.5 volts.
Correction from the velocity distribution curve, 10.30 − 9.56 volts.
Ionizing potential 8.50 + .74 = 9.24 volts.

Ethane.—Ethane was prepared by the action of ethyl iodide on alcohol in the presence of a zinc copper couple. The gas was passed through alcohol and then through concentrated sulphuric acid and was finally liquefied by liquid air. About five c.c. of the liquid were obtained. About a third of the gas was allowed to evaporate and the middle third was used to wash out the apparatus and to provide the sample for the experiment, the remainder being rejected.

Ionization curve: mercury vapor type.
Velocity distribution curve: oxygen type.

A. Pressure .0203 − .0176 mm.
Break point 8.60 volts.
Correction from the velocity distribution curve 9.92 − 8.52 volts.
Ionizing potential 8.60 + 1.40 = 10.0 volts.

B. Pressure .0109 − .0096 mm.
Break point 8.55 volts.
Correction from the velocity distribution curve, 9.92 − 8.52 volts.
Ionizing potential 8.55 + 1.40 = 9.95 volts.

Methane.—Methane was prepared by heating a mixture of sodium acetate and soda lime. The gas was passed through caustic soda solution and through concentrated sulphuric acid and was then liquefied. This was distilled, the middle portion being used to wash out the apparatus and to fill the supply bulb.

Ionization curve: hydrogen type.
Velocity distribution curve: hydrochloric acid type.

A. Pressure .0260 − .0221 mm.
Break point 8.22 volts.
Correction from the velocity distribution curve, 11.30 − 9.92 volts.
Ionizing potential 8.22 + 1.38 = 9.60 volts.

B. Pressure .0109 − .0096 mm.
Break point 7.8 volts.
Correction from the velocity distribution curve, 10.10 − 8.52 volts.
Ionizing potential 7.8 + 1.58 = 9.38 volts.

C. Pressure .0185 – .0168 mm.
Break point 7.9 volts.
Correction from the velocity distribution curve, 10.10 – 8.52 volts.
Ionizing potential 7.9 + 1.58 = 9.48 volts.

Acetylene.—Acetylene was prepared from calcium carbide and water. The gas was washed through caustic potash solution, a silver nitrate solution, and concentrated sulphuric acid. It was then solidified by liquid air. As in the case of carbon dioxide, fractional distillation from a solid is not likely to result in so pure a product as from a liquid.

Ionization curve: mercury vapor type.
Velocity distribution curve: hydrochloric acid type.

A. Pressure .0230 – .0212 mm.
Break point 8.80 volts.
Correction from the velocity distribution curve, 12.20 – 10.72 volts.
Ionizing potential 8.80 + 1.48 = 10.28 volts.

B. Pressure .0137 – .0130 mm.
Break point 8.4 volts.
Correction from the velocity distribution curve, 10.90 – 9.46 volts.
Ionizing potential 8.4 + 1.44 = 9.84 volts.

C. Pressure .0090 – ? mm.
Break point 8.30 volts.
Correction from the velocity distribution curve 10.90 – 9.46 volts.
Ionizing potential 8.30 + 1.44 = 9.74 volts.

Ethylene.—Ethylene was prepared from sulphuric acid and alcohol. The gas was passed through a condenser immersed in ice, caustic potash solution, and concentrated sulphuric acid. The gas was liquefied and distilled. The first third was allowed to boil away, the next was used to wash out the apparatus and fill the supply bulb, and the remainder was rejected. The gas used was probably very pure.

Ionization curve: mercury vapor type.
Velocity distribution curve: hydrochloric acid type.

A. Pressure .0336 – .0271 mm.
Break point 8.40 volts.
Correction from the velocity distribution curve 9.65 – 8.22 volts.
Ionizing potential 8.40 + 1.43 = 9.83 volts.

B. Pressure .0144 – .0130 mm.
Break point 8.40 volts.
Correction from the velocity distribution curve 9.70 – 8.22 volts.
Ionizing potential 8.40 + 1.48 = 9.88 volts.

Chlorine.—Chlorine was prepared by the action of sulphuric acid on potassium permanganate. It was liquefied by liquid air and distilled as usual. The electron current was unusually small, making it difficult to determine the exact position of the break point.

Ionization curve: oxygen type.
Velocity distribution curve: hydrochloric acid type.
Pressure
Break point 9.10 volts.
Correction from the velocity distribution curve 7.9 − 8.8 volts.
Ionizing potential 9.1 − .9 = 8.2 volts.

Bromine.—Bromine was introduced into a small tube in place of the supply bulb. Its own vapor pressure was sufficient to drive enough vapor through the capillary tube into the apparatus. As there was no stopcock between the bromine tube and the experimental part of the apparatus, it was unnecessary to cool the trap *T*. The bromine was condensed in the trap *S*, causing a constant flow of bromine vapor through the apparatus. The electron current was small in this experiment.

Ionization curve: mercury vapor type.
Velocity distribution curve: hydrochloric acid type.
Break point 10.5 volts.
Correction from the velocity distribution curve 8.1 − 8.6 volts.
Ionizing potential 10.5 − .5 = 10.0 volt.

Sulphur.—The ionizing potential of sulphur was not looked for directly, but in the course of the experiments, results were obtained which might be used with some justification to calculate the ionizing potential of sulphur vapor. In the experiment following that on hydrogen sulphide, some anomalous results were obtained, for on reducing the pressure to below .00001 mm. by the pump and preventing mercury vapor from entering the experimental tube by liquid air, a large electron current was still obtained. This result was quite contrary to what we had been led to expect from our other experiments. From one ionization curve, when corrected as usual, a value of 8.44 volts was obtained for the ionizing potential, and from another ionization curve a value of 8.24 volts was obtained. That this is probably due to sulphur may be inferred from the fact that there was no appreciable amount of gas or mercury vapor in the experimental tube, and also that on heating the experimental tube at the end of the observations some sulphur was driven out. This had probably been the result of a partial decomposition of the hydrogen sulphide by the hot filament. On cutting down the experimental tube and cleaning out the sulphur by heating in a current of air, and repeating

the experiments again, it was found that the source of the ionization curve was removed and normal results were obtained. These values, attributed to sulphur, hardly deserve as much credit as the other results.

SUMMARY OF RESULTS.

The results are summarized in the following table, in which the values of the ionizing potentials are given to the nearest tenth of a volt. One can hardly claim an average accuracy of more than about .2 or .3 volt, as it is difficult to say exactly where the ionization curve begins and where the velocity distribution curve cuts the axis. (Theoretically, of course, it never actually cuts the axis.) However, for purposes of comparison between the different gases, one can probably claim an average accuracy of about .2 volt.

Ionizing Potentials.

Gas.	This Investigation.	Franck and Hertz.	Goucher.	Bazzoni.	Compton's Theory.	Atomic Volumes.	Atomic Radii.
He.....	—	20.5	—	20.0	22.8	23.5	1.11×10^{-8}
Ne.....	—	16	—		16.8	19.2	—
A.....	—	12	—		8.2	28.0	1.81
H_2.....	10.2	11	10.25?		11.8	9.2	1.34
O_2.....	9.2	9	—		8.4	11.2	1.81
N_2.....	7.7	7.5	7.4		8.05	13.7	1.90
S.....	8.3?		—		4.25	15.5	—
Cl_2.....	8.2		—		4.94	21.4	2.68
Br_2.....	10.0		–		—	25.6	—
Hg.....	10.2		10.0		4.65	14.8	—
HCl.....	9.5				6.50		—
CO.....	7.2				—		1.88
CO_2.....	10.0				6.47		2.28
NO.....	9.3				—		1.86
CH_4.....	9.5				6.54		—
C_2H_6.....	10.0				—		—
C_2H_4.....	9.9				—		2.75
C_2H_2.....	9.9				—		—

The experimental results obtained by Franck and Hertz, by Goucher, and by Bazzoni, are shown in the table. Where comparison is possible, there is good agreement. The values predicted from Compton's theory[1] are also given in the table. In the last two columns will be found the atomic values taken from a paper by Harkins and Hall,[2] and the atomic radii taken from Jeans's Dynamical Theory of Gases (2d edition, p. 341).

[1] Compton, PHYS. REV., VIII., p. 412, Oct., 1916.

[2] Harkins and Hall, Am. Chem. Soc. Jour., XXXVIII., p. 169, Feb., 1916.

DISCUSSION OF THE RESULTS.

Shape of the Ionization Curves.—The variations in the shape of the ionization curves are greater than can be accounted for by differences in the velocity distribution curves. This implies that the way in which the ionization by collision depends upon the velocity of the electron (above the ionizing potential) differs for different cases. If we assume that the ionization per collision is constant for velocities above the ionizing potentials then it can be shown that the straight part of the curve, when produced, intersects the axis at a point which gives approximately the ionizing potential, provided we refer this point to the voltage corresponding to the most probable energy of the electron, and not as we have done hitherto, to the energy of the fastest electrons. Such is the case for ethylene, and approximately so for mercury vapor, but not at all the case for oxygen. (Some of the curves have no straight portions.) As these experiments were not designed primarily to investigate this relation, the matter will be left without further comment.

Ionizing Potentials of the Elements.—A knowledge of the ionizing potentials of the elements should furnish material for testing theories of atomic structure. The only theory which is sufficiently well developed to enable us to make a quantitative comparison is that due to Bohr,[1] and even Bohr's theory is only worked out in sufficient detail to allow us to test the results for hydrogen and helium.

Bohr pictures a hydrogen atom as one electron rotating about a positive nucleus possessing one unit positive charge. The only orbits which are possible are those in which the electron has angular momentum equal to some integral multiple of $h/2\pi$. The negative energy of the atom is

$$W = \frac{2\pi m e^4}{h^3}\,\frac{1}{\tau} = K\frac{1}{\tau},$$

where τ is the number of the orbit, being 1 for the innermost orbit, 2 for the next, and so on, and K is Rydberg's constant, 3.29×10^{15}. This will give the energy required to remove the electron from the orbit to infinity. The work required to remove the electron from the mth orbit to the nth is

$$K\left(\frac{1}{m^2} - \frac{1}{n^2}\right).$$

For purposes of comparison with experiments, it is convenient to express the work in terms of equivalent volts. On this basis, K corresponds to 13.5 volts, and this measures the energy required to remove the electron

[1] Bohr, Phil. Mag., XXVI., p. 857, Nov., 1913.

from the innermost ring. We should expect this to represent the energy necessary to ionize the normal atom. The work required to move the electron from the first to the second ring would be

$$K\left(\frac{1}{1^2}-\frac{1}{2^2}\right), \quad \text{or} \quad 10.1 \text{ volts.}$$

This is very close to the ionizing potential of hydrogen as found by experiment, but does not, on the other hand, represent the work required to remove an electron completely, which we should naturally consider to be the work of ionization.

It might be argued that we are working with the hydrogen molecule and not with the hydrogen atom. According to Bohr, the molecule may be pictured as two positive nuclei with two electrons rotating about the line joining them. Each electron has angular momentum equal to some multiple of the constant of angular momentum. The molecule in its normal state has unit angular momentum for its electrons. The negative energy of such a molecule is $2.20K$ and the negative energy of such a molecule with one electron completely removed is $.88K$. The work required to remove the electron is therefore

$$2.20K - .88K = 1.32K, \quad \text{or} \quad 17.7 \text{ volts.}$$

Bohr however shows that the positively charged molecule is unstable, and prefers to regard the ionization of the hydrogen molecule as the disintegration of the molecule into a single nucleus and a hydrogen atom. This requires energy of the amount

$$2.20K - K = 1.20K, \quad \text{or} \quad 16.2 \text{ volts.}$$

Bohr pictures the normal helium atom as two electrons rotating round a doubly charged positive nucleus, each electron having angular momentum equal to some multiple of the unit angular momentum. The negative energy of the normal helium atom, the electrons being in the innermost ring, is $6.13K$, and the negative energy of the positively charged helium atom, with one electron in its innermost orbit, is $4K$. The work to remove one electron is therefore

$$6.13K - 4K = 2.13K, \quad \text{or} \quad 28.6 \text{ volts.}$$

The work to remove one electron, not to infinity, but to the next orbit, will be some fraction of this. Its value will depend upon the assumptions as to the rearrangements of the orbits; we may probably assume that it will not be very different from 3/4, the value previously obtained

for the hydrogen atom. This gives 21 volts. It is significant that the ionizing potentials of hydrogen and helium do not agree with the values calculated for the complete removal of an electron from the respective atoms, but do seem to agree with the values of the energy required to move an electron from the innermost ring to the next. Moreover, the experiments of Bazzoni show no traces of any extra ionization setting in at 28.6 volts, nor do our experiments show any discontinuity in the curves for hydrogen at 13.5 volts or at 16.2 volts. It may be inferred that the ionization does not consist of the direct expulsion of an electron from an atom by the impact of another electron, but, as Bohr has suggested in the case of helium, is the result of a transition from the normal state of the atom to the next stationary state. This may come about in several ways. To test whether ionization consists in the transfer of an electron from the innermost orbit to the next, followed by a complete removal from that orbit by a second collision with an electron, we measured the ratio of the ionization currents to the electron currents. If we assume that atoms with electrons displaced to the second orbit tend to go back to the normal state, then, if the electron current is small, almost all the atoms will go back to their normal state before they are hit a second time, while if the electron current be large, there would be a much greater chance for an atom to be struck a second time before it had got back to its normal state. Our experiments showed that the ionization current was doubled when the electron current was doubled, and therefore this linear relation gives no support to this particular view of the mechanism of ionization.

For gases other than hydrogen and helium, we must do without so definite a theory and content ourselves with searching for general relations. There is no clear connection between the ionizing potential of an element and its electronegative or electropositive character. On Bohr's theory we have seen that the closer the electron is to the nucleus, the more is the energy required to take it away. We might therefore try the effect of comparing the ionizing potential with the radius of the atom. Provided we keep to elements which are not too widely separated in character, an increase in atomic volume and atomic radius is accompanied by a decrease in the ionizing potential. This is the case for the inert gases, if we disregard neon, as its atomic volume is not so well established as that of the other gases. It is also the case for hydrogen, oxygen, and nitrogen. It is not the case however for bromine and chlorine. It is well to remember that the experimental difficulties were greater in the case of these gases than in the case of other gases. This relation is similar to one noticed by one of the authors,[1] viz., that there is

[1]Hughes, Phil. Trans., CCXII., p. 205, 1912.

a regular decrease in the energy required to detach a photo-electron from a metal as the atomic volume increases. This relation holds only for elements within the same column of the periodic table; there is a discontinuity (always in the same direction, however) as we pass from one column to the next. A close relation between the atomic radius and the ionizing potential for all the elements could hardly be expected, as the arrangement of the electrons in the atom must be a factor in determining the energy required to detach an outermost electron in addition to the radii of their orbits. According to Ludlam[1] chlorine is not ionized by the ultra-violet light which is capable of ionizing air. This is in agreement with these experiments if the ionization of air by ultra-violet light is due to the ionization of nitrogen alone, but not so if the oxygen is ionized as well.

Compton[2] recently proposed a theory from which he deduced a relation between the ionizing potential V and the specific inductive capacity K of a gas.

$$V = \frac{.194}{\sqrt{K-1}}.$$

This formula agrees fairly well for most of the elements; the agreement is poor however for mercury, chlorine, and sulphur, if our value be correct.

Ionizing Potentials for Compounds.—The results do not point to any definite relations for compounds. The ionizing potential for hydrochloric acid is intermediate between that of hydrogen and that of chlorine. The same relation holds for hydrogen disulphide, hydrogen, and sulphur, but does not for oxygen, nitrogen, and nitric oxide. In working on the photo-electric effect of solid compounds[3] it was noticed that, in general, the more stable the compound (measured by its heat of formation) the less was its photo-electric effect and presumably the more difficult it was to detach an electron. It might be reasonably expected therefore that the ionizing potentials would be greater for the more stable compound gases. On testing this out no sort of agreement could be found. Indeed, the ionizing potential is almost constant for the four hydrocarbons, two of which are exothermic and two endothermic.

The values of the ionizing potentials calculated from Compton's theory, are little more than half the experimental values. Compton does not expect a good agreement on account of the uncertainty in the values of the specific inductive capacity K for the compound gases.

[1] Ludlam, Phil. Mag., XXIII., p. 757, 1912.

[2] Compton, Phys. Rev., VIII., p. 412, Oct., 1916.

[3] Hughes, Phil. Mag., XXIV., p. 380, 1912.

SUMMARY.

The ionizing potentials of fifteen gases have been measured by a method similar in principle to that of Franck and Hertz. A second method of measuring the ionizing potential was worked out, but gave satisfactory results only in the case of mercury vapor.

The ionization of mercury vapor by electrons whose energy is somewhat greater than that corresponding to the ionizing potential is much more intense than is the case for the other gases.

Several relations which might be expected to account for the values of the ionizing potentials have been suggested. The experimental values, however, do not agree well with any of them.

A DETERMINATION OF THE PLANCK RADIATION CONSTANT C_2.

BY C. E. MENDENHALL.

THE cross-connections of Planck's radiation theory give an importance and interest to its constants which is sufficient excuse for devoting a considerable amount of time to their accurate determination. The work to be described in the present paper involves some novelties of method and conditions and some refinements of observation which it is hoped have led to an increase in final accuracy. The work will be discussed in two parts, in both of which however, the same method was used, namely, that involving the measurement of the ratio of the intensity of emission for a known wave-length at two known temperatures. For the wave-lengths and temperatures involved the Planck equation

$$E = c_1\lambda^{-5}\frac{1}{e^{C_2/\lambda T} - 1}$$

is equivalent to the Wien form

$$E = c_1\lambda^{-5}e^{C_2/\lambda T}$$

to less than one part in ten thousand. Using the Wien form, the ratio of intensities is given by

$$\log\left(\frac{E_{T_1}}{E_{T_1}}\right) = \frac{C_2}{\lambda}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

In the first part of the work, a graphite tube furnace was used, and T_2 (2705° K.) was determined from T_1 (1604° K.) by the use of the Stefan Boltzman law. The general arrangement of the furnace and some of its attachments are shown in a previous paper.[1] The methods used in determining the observed quantities, λ, E_1/E_2, T_1 and T_2 will first be considered.

1. The wave-length used was determined by an ocular slit in the focal plane of a Hilger constant deviation spectroscope. The slit subtended about 20 Ångströms, and its center was found by careful calibration, to be at 6501 Å.U.

2. The ratio E_1/E_2. In front of the collimator slit of this instrument

[1] Mendenhall and Forsythe, PHYS. REV., 2d series, Vol. IV., p. 65, July, 1914.

was mounted a pair of achromatic lenses and a comparison lamp. The first lens served to form an image of the black body diaphragm in the furnace, in the plane of the lamp filament, while the second formed an image of this image and of the filament upon the spectroscope slit. The arrangement is thus a spectro-optical pyrometer, the comparison field consisting of a narrow band in the center from the comparison filament, bordered above and below by light from the furnace. By careful adjustment one very sharp separating line was obtained, permitting adjustments of very considerable accuracy. The brightness of the comparison filament was determined by reading the current flowing through it, on a Siemens & Halske millivoltmeter provided with such a shunt as to give nearly a full scale deflection, and read with a magnifying glass. In this way the current necessary to give photometric balance against the furnace at the temperature T_1 was determined. With the furnace at the high temperature T_2 a large rotating sector (12 inches in diameter) was inserted in front of the first lens so as to reduce the intensity of the light from the furnace. This disc had two apertures, either of which could be closed by pasting over a piece of black paper. One aperture reduced the intensity of the furnace light to a value slightly greater, the other to a value slightly less than the initial intensity at temperature T_1. One aperture had an opening of 1° 17′ 05″, the other an opening of 1° 12′ 18″. Thus by determining the lamp current required to give photometric balance with each of these apertures in turn, it was possible by linear interpolation, plotting lamp current against the logarithm of the sector reduction factors, to determine the aperture which would have reduced the $E_{\lambda T_2}$ exactly to the $E_{\lambda T_1}$. The quotient of 2π by this aperture (in radius) is the ratio E_2/E_1. The value of the sector apertures was determined by very careful measurements on a Geneva Society spectrometer. The losses at the glass window W, provided they remain constant at T_1 and T_2, obviously do not enter into this matter. The linear interpolation referred to above between the two sectors was shown to be allowable by determining the intensity of emission I of the comparison lamp as a function of current, and plotting log I against current. The resulting curve had such a slight curvature that for the small range between the two sector apertures straight-line interpolation was quite sufficient.

3. The temperature T_1. This temperature was defined and reproduced as that having 14.91 times the intensity of radiation of a black body at the melting point of gold, for the complex of wave-lengths transmitted by two thicknesses of the standard red pyrometer glass No. 2745. This temperature was chosen because it gave an intensity of light permitting

about the maximum accuracy of photometric balancing, with the spectroscopic outfit described above. It was practically realized by calibrating a pyrometer at the gold point using a platinum-wound black-body furnace and determining the melting point by the wire method. This pyrometer was then put in front of the graphite tube furnace, in place of the spectro-pyrometer, a sector with a transmission ratio 1/14.91 rotated in front of it, and the furnace temperature raised until the pyrometer indicated the correct gold point, the losses due to the glass window W having been allowed for in the calibration. At the same time a control pyrometer was sighted into the back of the furnace, and its reading obtained when the proper temperature was reached as shown by the front pyrometer. Of course this transfer or comparison was carried through several times in connection with each "determination" of c_2, and before and during the series two very consistent determinations of the gold point with the "front" pyrometer were carried out. After the temperature T_1 had thus been transferred to the back or control pyrometer, the front pyrometer was lifted away and replaced by the spectroscope.[1] The actual determination of the value of T_1 defined as above was accomplished some time later, using a standardized thermo-couple borrowed from the geophysical laboratory through the kindness of Dr. Day. For the constants of this particular couple and for very valuable suggestions as to the proper use of it, I am under obligations to Dr. W. P. White. The same pyrometer and lamp was of course used, with two different black body furnaces, and many determinations of the gold point were made in this connection. As this determination of T_1 is of fundamental importance, and as it is not altogether simple even granted a standardized couple, it must be considered a little more in detail. The first furnace used, double wound with platinum on Marquardt porcelain tubes, was almost exactly the same length as that in which Dr. White had determined the constants of the couple, and the couple gave almost exactly its standard E.M.F. at the gold point. The remaining descrepancy might be due to a difference in the furnace gradient, a difference between the wire and crucible methods of determining melting points, a difference in the purity of the gold, or a difference between the two potentiometer and standard cell combinations. The last two factors were eliminated by using a little gold wire from the geophysical laboratory, which gave the same melting point as ours, and by measuring on our potentiometer the E.M.F. of a number of copper-constantin couples

[1] It may be asked why the "control" or back pyrometer was not itself used to determine the initial temperature; but it is evident that it is the temperature of the *front* face of the interior graphite diaphragm that is desired, since it is at this face that the spectroscope and the Stefan Boltzman apparatus both point.

arranged to have one junction in melting ice and the other in steam. This is a standard arrangement of Dr. White's for comparing potentiometers. My values for the E.M.F. of this " tester " indicated that my potentiometer read about 1/5500 high. As there was already considerable evidence that the wire and crucible methods give consistent values for the melting point, this matter was not gone into, but it was concluded that the difference between our value and the standard E.M.F. of the couple at the gold point was due to a difference in furnace gradient. This difference in E.M.F. may conveniently be referred to as the " furnace correction." With the first furnace it amounted to only about $2\mu v$ (.15° C.), and it was assumed not to vary with temperature from the gold point up to T_1. Some justification for this assumption will be referred to later. The optical pyrometer used in the C_2 observations was now used to determine a temperature of this furnace for which the intensity of radiation through the double red filter (No. 2745) was 14.91 times that at the gold point, and the E.M.F. of the standard couple at this temperature measured. The " furnace correction " was applied to this to reduce to standard conditions—and from this the temperature was determined. In this way five independent determinations of T_1 were made with this furnace as follows: 1332°.1, 1331°.9, 1330°.9, 1330°.1, 1330°.2, mean 1331°.0 C. A longer furnace was next used, and the hot end of the couple extended by wire taken from the other end so as to bring the temperature gradient as nearly as possible along the same part of the wires. The standard conditions were not so well reproduced in this furnace as in the other, as the " furnace correction " was now about $10\mu v$ (.8° C.). The windings of this furnace were in bad condition, however, as was evident from the variations in the determinations of the gold point, and only three determinations were made before it was necessary to repair it. They were not as consistent as the first, and the mean is considerably lower, 1328°.9 C. Owing to the bad condition of the furnace, and to the fact that the furnace couple was found, upon taking apart for repairs, to have been misconnected, very little weight is given these results in the final average. While repairing this furnace opportunity was taken still further to improve it by lining the innermost " black body " chamber with platinum of sufficient thickness to increase the uniformity of temperature. The " black body " chamber of this furnace was about 4 cm. long, and 1.5 cm. in diameter, with an aperture about 4 mm. in diameter. As indicated by the lack of any optical definition in the interior, and small difference in brightness between the aperture and the diaphragm containing the aperture, the black body conditions must have been very good indeed, as would be expected since

the aperture was less than 1 per cent. of the internal radiating area. There was no difference between the radiation measurements in the two furnaces at the gold point. With the repaired furnace, which gave beautifully consistent values for the gold point, three more determinations of T_1 were made, giving 1332°.0, 1330°.8, 1330°.9 C. Giving these, for the reasons mentioned above, very considerably more weight than the preceding three, the mean for the long furnace is 1330°.6 C., and the close agreement of this with the mean for the short furnace is considered to be some justification for the assumption that the " furnace correction " is independent of temperature. Finally the mean value obtained for T_1 is 1330°.8 C., or with all the accuracy that may be claimed here, 1331° C., which is believed to be correct to 0°.5 C.

4. T_2. As has been previously described, the front part of the graphite tube furnace chamber contained a thermopile, consisting of a single junction with a thin blackened silver receiving surface, 3 mm. in diameter at the center of a small hemispherical silver mirror, to increase the effective absorbing power. This was connected to a suitable D'Arsonval galvanometer so that when exposed to the total radiation from the furnace at temperature T_1 a deflection of from 30 cm. to 40 cm. would be obtained. By means of the control pyrometer and a suitable choke coil in the primary of the transformer supplying the furnace, it was possible to hold the temperature constant while these thermopile readings were being obtained. In order to determine the temperature T_2, a rotating sector of suitable aperture could be swung into place in the furnace chamber between the pile and the graphite black body furnace, and the temperature of the furnace raised until upon exposing the pile, the same deflection as before was obtained. If S is the transmission coefficient (*i. e.*, ratio of angular opening to 2π), then according to the Stefan Boltzman law we have $T_2 = T_1 \sqrt[4]{1/S}$. In the meantime a suitable rotating sector would be mounted in front of the control pyrometer, so that a reading of the temperature of the back of the furnace could be obtained, corresponding to T_2 at the front. A somewhat fuller description of this part of the apparatus, designed for the measurement of temperatures by the Stefan Boltzman law, will be found in a previous article. It need only be mentioned here that the requisite diaphragms and shutters were water cooled, and the sectors inside B were made double so as to avoid any danger of their heating up and re-radiating to the thermopile. A steady flow of nitrogen at about 12 mm. pressure was maintained through the furnace chamber, and it has been found by previous tests that the absorption of such an atmosphere was quite negligible. It should be mentioned that the tests for absorption were made with

furnace gases drawn out into a side tube and hence cold; but I know of nothing to indicate that the absorption would be greater when hot. The succession of operations incident to a single determination of C_2 may now be summarized as follows: First, the standard pyrometer was directed into the front of the furnace, with a 14.91 sector rotating in front of it. The furnace temperature was raised until the pyrometer indicated the gold point. The spectroscope and attachments were then substituted for the pyrometer, and the lamp current necessary to balance against the furnace (with no sector) was carefully determined. Then the galvanometer deflection (about 350 mm.) due to the total radiation thermopile (with no sector) was measured. The temperature of the furnace was then raised until the same deflection was obtained with the 1/8.331 sector rotating in front of the thermopile. Then the large sector was rotated in front of the spectroscope, and the lamp current determined, which would give photometric balance with each of its two apertures exposed in turn. In two instances it was not possible to obtain satisfactory observations with both apertures, and for these cases the slope of the log I, current curve was taken from the work of the preceding and following days.

Results.—Six series of this sort were carried out, each giving a value of log E_2/E_1 as follows:

2.468	2.469	
2.464	2.466	Mean, 2.4663.[1]
2.466	2.465	

The agreement may be considered extremely satisfactory, the extreme range corresponding to values of c_2 of 14,381 and 14,410. Gathering together the data for the determination of c_2 we have, corresponding to the expression $c_2 = \log R(\lambda T_1 T_2/T_2 - T_1)$, $\log R = 2.4663$, $\lambda = 6{,}501$, $T_1 = 1{,}604$, $T_2 = 2{,}725$, from which $C_2 = 14{,}394$.

Sources of Error.—(*a*) Wave-length. The error in the determination of the wave-length corresponding to the center of the ocular slit is negligible, certainly not more than one Ångström, but there is always the danger of scattered light of shorter wave-length to which the eye is more sensitive. The high dispersion of the Hilger prism ($\mu_D = 1.74$) the narrow slits used, and the relatively long interval from the region of maximum eye sensibility to the wave-length used all tend to minimize this source of error.

[1] In addition an earlier set in which the temperatures were measured through the back or control end of the furnace gave log $R = 2.467$.

(*b*) In T_1. Since an error of an entire degree in T would only produce an error of 1 part in 1,600 in C_2, no very great error is to be expected from this source, unless it arises from some change in the pyrometer occurring between its use in the main part of the work, and the determination of T_1 by thermocouple comparisons. And since the same red glass eye screens were used in both cases, it is difficult to see how even a change in the pyrometer could seriously affect the result. Further evidence of the accuracy of the determination of T_1 is given by the application of Wien's law to the red glass optical pyrometer between the gold point and T_1. Using for the effective wave-length of transmission of the double thickness of glass No. 2745, as determined by Hyde Cady & Forsythe, $\lambda = .6671\mu$ for C_2 the value above given, and for the ratio of intensities the measured sector ratio 14,908, the resulting value of T_1 is 1331°.4 C. This is certainly as close an agreement as could be expected.

(*c*) T_2. There are here several possible sources of error. First, the fact that the thermopile receiving surface was not perfectly absorbing would enter only as a second order error, due to a possible difference in the effective absorbing power at the two temperatures T_1 and T_2 resulting from the change in the spectral energy distribution. No attempt was made to determine the magnitude of this error, but as the maximum of energy in the black body spectrum shifts only from about 1.8μ to 1.0μ for these two temperatures and as the absorbing power of acetyline black is almost independent of wave-length in this region, it seems safe to conclude that the error in question would be very small. The absorption of the gases in the furnace chamber (12 mm. pressure) would also produce only a differential error, and as before stated it had been found that the total absorption of these gases when cold, was certainly not more than 0.1 per cent. The sectors used in front of the thermopile were of large aperture and could be readily measured with the necessary accuracy. The galvanometer deflections of about 350 mm. could be read to 0.1 mm. and they were so consistent and reproduceable as to give one great confidence in their reliability. The question of galvanometer proportionality did not enter, as the same deflection was used at T_1 and T_2.

(*d*) R, the ratio of emissivities. In this connection the most difficult factors to determine were the two sector apertures of 1.284, and 1.205. In measuring these the smallest angle which could be read, by estimation, was 5″. As each aperture was measured five times and each measurement read on two verniers it would seem safe to expect an accuracy of at least one part in a thousand in the final value, especially in the average of the two, which is really what counts.

Summing up, it does not seem unreasonable to hope for an accuracy of one part in five hundred in the final result.

THE SECOND METHOD.

This was exactly the same in principle, but applied directly between the melting points of gold and palladium as determined by the wire method. This simplifies the temperature measurements, but the temperature range is so much less that the temperatures must be known with greater accuracy, and the intensity of emission is so low at the gold point that photometric balancing is far less accurate. In fact this work was carried out merely as a check on that already described, to show that the value of C_2 obtained above was consistent with observations at the lower temperatures. The various elements of the problem will be briefly discussed.

The Furnace.—This was the long one referred to above, with a platinum lining on all walls of the radiating chamber but the rear one at which the pyrometers were sighted. Its extreme length was 70 cm., and the temperature gradients were so small in the central chamber that five gold melts would as a rule all fall inside an interval of .6° C. and five palladium melts in an interval of 2°.0 C. Only the purest Hereans gold and palladium were used, and melting points were determined at short intervals, so that the changes in the thermocouples which occurred at every heating to the palladium point (1549° C.) should be as much as possible eliminated. The form of spectro-pyrometer previously used was remodeled and improved for this work. The most serious source of error is the optical defects of the comparison lamp bulb which diffuse the dividing line between the two fields. A strip of thin platinum in air gave much more accurate balancing conditions, but was not sufficiently permanent. It is hoped to make improvements in this feature. The ratio of intensities was again determined by interpolation between sectors, on the log I current curve. Two different wave-lengths were used, 0.5780μ and 0.5460μ, chosen at the yellow and green mercury lines so that the wave-length scale could be quickly checked. The collimator slit covered about 20 Ångströms and the ocular slit about 20.

Results—The values of C_2 cover a considerable range, as was expected, and hence a considerable number, 17, separate determinations were made. Aside from the wave-length other conditions such as aperture of image-forming beam, and width of collimator slit were varied, without producing much systematic change in the result. The individual values are as follows: 14450, 14416, 14400, 14460, 14450, 14300, 14450, 14450, 14206, 14455, 14411, 14506, 14453, 14506, 14455, 14355, 14291.

While these results vary in a disappointing way, still the mean 14,413 is in about as close agreement as could be expected with the value found under the very different conditions first described. Comparing the

values of C_2 obtained with $\lambda = .667\mu$, $.577\mu$ and $.546\mu$, there is slight evidence of a dependence of the value obtained upon the wave-length used, but considering the uncertainty of the second method it is not wise to attach any significance to this. As a final value, less weight being given to the second series of observations, the round number 14,400 is perhaps satisfactory.

Recent values to be compared with this are:

Reichsanstalt[1].....14,300,
Coblentz[2].....14,322 and 14,369,
Hyde, Cady & Forsythe[3].....14,460.

Of these the latter is subject to the added uncertainty of having been determined directly with red glass screens which are very far from monochromatic. The present value falls in the middle of the range of recent measurements, but differs from the results of the other most direct determinations by much more than the supposed limit of error of any of them.

THE RELATION OF C_2 TO OTHER CONSTANTS.

According to Planck's theory C_2 is related to a number of other constants by the following equations:

$$\lambda_m T = \frac{C_2}{4.9651}, \quad h = \frac{aC_2^4}{48\pi\alpha C}, \quad k = \frac{aC_2^3}{48\pi\alpha},$$

where

$a = 4\sigma/c$ = constant of total radiation.
h = Planck's quantum constant.
k = Planck's probability constant.
α = 1.0823.
c = vel. of light.

These equations give opportunity for three cross-connections or checks, of which only the last two need be considered. It is of most interest to compare the values of h and k determined by purely radiation observations with the value of h determined by Millikan from photo-electric methods, and the value of k computed by Millikan from his value of e, the electric charge, and the gas constant R. In order to do this I have used Westphall's latest value for σ as quoted by Millikan namely, 5.67×10^{-12} (watts/cm.^{2} Deg.^{4})

[1] Mueller, Warburg et al., Ann. Phys., 48, 1915, 430.
[2] Coblentz, PHYS. REV., 7, 1916.
[3] Hyde, Cady and Forsythe, Ap. J., June, 1915.

Using $C_2 = 14{,}400$ the resulting values are:

$$h = 6.654 \times 10^{-27},$$
$$k = 1.383 \times 10^{-16}.$$

Whereas Millikan's values are:

$$h = 6.547 \times 10^{-27},[1]$$
$$k = 1.372 \times 10^{-16},[2].$$

On the other hand, combining Millikan's value of k with the present C_2, gives $h = 6.585 \times 10^{-27}$, which is in better agreement with Millikan's photo-electric value.

If Coblentz's value of σ, 5.72×10^{-12} be used, discrepancy between the *radiation* and the *electrical* values of h and k become still larger. The contrast is put in the reverse way by Millikan, who computes from electrical and gas data the values $C_2 = 14{,}312$ and $\sigma = 5.72 \times 10^{-12}$. It will be observed that this value of C_2 is well at the extreme of the range of recent direct experimental results, while the value for σ agrees exactly with Coblentz and very closely with Westphall.

It remains for further work to decide as to the significance of these discrepancies.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF WISCONSIN,
May, 1917.

[1] Millikan, Proc. Nat. Acad. Sci., April, 1917.
[2] Millikan, PHYS. REV., 2, 1913, pp. 109–143.

A DETERMINATION OF THE RATIO OF THE SPECIFIC HEATS OF HYDROGEN AT 18° C. AND − 190° C.

BY MARGARET CALDERWOOD SHIELDS.

THE method for determining the ratio of the specific heats of gases originally presented by Lummer and Pringsheim[1] in 1898, and since used in modified form by Moody[2] and by Partington,[3] is generally conceded to be the most precise method thus far available, its only disadvantage being that it has seemed to require large quantities of gas. Three years ago, however, H. N. Mercer[4] obtained with the use of surprisingly small flasks some preliminary data which pointed to the possibility of using the method with small scale apparatus. Accordingly Professor Millikan suggested to the author two problems which were obviously waiting such an opportunity.

First: There are in the literature of the subject at present only two satisfactory determinations of the ratio for hydrogen at 20° C.; 1.4084, a direct determination by Lummer and Pringhseim, and 1.407, computed by Scheel and Heuse[5] from their observations on C_p by the "constant flow" method. Inasmuch as the kinetic theory affords no explanation of values so high, and experimental data generally are now under close examination from the point of view of the quantum theory, a careful redetermination of the ratio is needed to decide whether a quantum effect is actually manifested in hydrogen at this temperature.

Second: Eucken,[6] from observations on C_v, and Scheel and Heuse from observations on C_p, have announced that the hydrogen molecule loses almost entirely its two degrees of rotational freedom by the time the temperature reaches − 180° C., and becomes virtually a monatomic gas, the ratio of the specific heats being according to Eucken 1.604, and according to Scheel and Heuse 1.595. Will it be possible to confirm this by direct observation of the ratio?

This paper is an attempt to answer these two questions.

[1] Ann. d. Phys., 64: 536, 1898.
[2] PHYS. REV., 34: 275, 1912.
[3] Phys. Zeit., 14: 969, 1913.
[4] Pro. Roy. Soc. London, 26: 155, 1914.
[5] Ann. d. Phys., 40: 473, 1913.
[6] Ber. d. Preus. Akad., 1912, p. 141.

I. At 18°.

Experimental Arrangements.—The method employed for this investigation is, as stated above, essentially that of Lummer and Pringsheim. It consists in measuring the cooling attendant upon an adiabatic expansion from p_1 to p_2; the two pressures and temperatures are connected for the ideal gas by the relation,

$$\left(\frac{p_1}{p_2}\right)^{\gamma'} = \left(\frac{\theta_1}{\theta_2}\right)^{\gamma} \tag{1}$$

and γ is therefore obtained from the equation,

$$\gamma = \frac{\log {}^{p_1}/_{p_2}}{\log {}^{p_1}/_{p_2} - \log {}^{\theta_1}/_{\theta_2}}. \tag{2}$$

The two modifications of the original experiment are (1) the use of a one liter flask in place of a large carboy, and (2) the substitution of a minute thermojunction for the platinum resistance thermometer, following in this respect the method already used by Moody in the Ryerson laboratory.

The thermal element was of .001 inch copper and constantan wires. It was introduced into the flask by means of two glass tubes through the rubber stopper, which were inside drawn out to fine capillaries and bent into a Y, which spread nearly to the diameter of the bulb, and could be folded together for insertion into the flask by twisting each of the tubes through 90°. It was found by repeated effort that normal values of γ could be obtained only when the couple was thus introduced with a minimum of glass as remote as possible from the junction, and the junction itself placed carefully at the center of the flask. The junctions were brazed in the edge of a Bunsen flame by holding in metal tweezers immediately back of the point to be brazed. Outside, the tubes ended in capsules containing the junctions with the copper lead-wires; these dipped into the water bath containing the bulb. The tubes were sealed by a mixture of beeswax and resin where they opened into the flask.

The arrangement by which the gas was sent into the flask is shown in Fig. 1. Air was taken from the laboratory compressed air system, passed through two bottles of concentrated sulphuric acid, then over a considerable length of solid caustic soda to remove carbon dioxide, and finally over phosphorus pentoxide. Hydrogen was obtained electrolytically and passed through the same system; further purification was deemed unnecessary, in view of the fact that the question of density is not involved in the experiment. The pressure gauge, *O*, on which the excess pressure was read, is of tubing 2.5 cm. in diameter, filled with light

transformer oil. With cocks *a* and *c* closed, the mercury could be raised in *R* to just the right height as indicated by the accessory mercury gauge, *M*, so that on opening the cock *c*, the oil moved less than a centimeter. There is thus practically no change in the gauge reading after the bulb is filled, due to hanging of oil on the walls. The inverted U-tube through

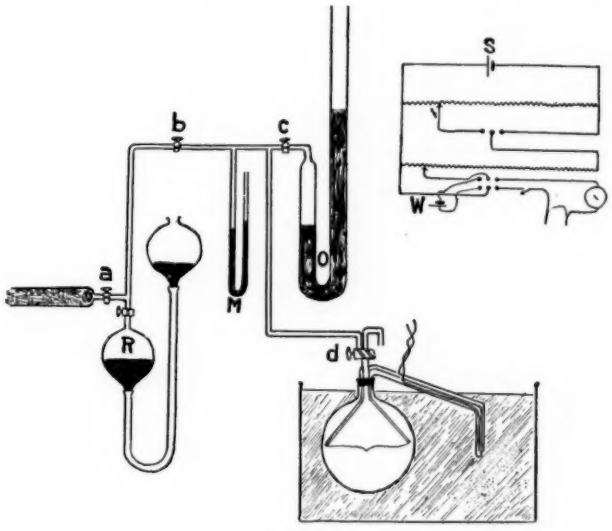

Fig. 1.

which the expansion takes place serves in the case of hydrogen as a trap to prevent air from being carried back into the bulb during the surges incident to the expansion.

The thermal E.M.F. developed by the expansion was measured by a null method with a Wolff potentiometer. An E.M.F. of the order of .002 volt was applied from a storage cell which was compared with a Weston standard before and after each series of observations. A ballistic galvanometer of the D'Arsonval type was used. It was read by a telescope and scale at a distance of 3.6 meters; the angle of deflection was doubled with practically no loss of light by the simple device of throwing the beam back upon the galvanometer mirror from a small stationary mirror about 10 cm. in front of it. Under these conditions the galvanometer sensibility was such that 3.8×10^{-8} volts corresponded to 1 mm. deflection. The constant of the thermojunction between 0° and 20° is 3.707×10^{-5} volts per degree; consequently an equilibrium temperature could be read directly to .001° and estimated to .0002°. In order to eliminate spurious motion it was found necessary to mount the galvanometer on a Julius suspension,[1] which was built very nearly

[1] Ann. d. Phys., 56: 151, 1895.

according to the original specification, the whole platform weighing about 11 kg.; the situation proved too severe a test of even this admirable device, so that observations were made only during the quieter portion of the day.

The method of procedure for a single determination was as follows: The bulb was filled and the cock *b* closed at some definite pressure, 10 to 50 cm. of oil in excess of atmospheric pressure. The potentiometer was kept balanced till it was certain that the gas had attained the temperature of the bath. Then the thermojunction circuit was opened, and the potentiometer resistance across which it is shunted changed to one or two ohms less than that which would presumably balance the E.M.F. developed by the expansion. The two-way cock, *d*, was turned to cut off the pressure gauge; then on one beat of a metronome, *d* was turned to open the bulb to the atmosphere, and on the next beat the potentiometer was closed. An instant backward throw of the galvanometer of 1 to 5 mm. is observed before it starts forward with rising temperature. The pressure gauge is read immediately, and the process is repeated for identically the same pressure with a potentiometer resistance different by an ohm. From six to ten such observations are used to fix a line from which the equilibrium resistance may be found by extrapolation. Data for one such observation are shown in Table I.

TABLE I.

p_2.	Δp.	ΔT.		T.
		Potentiometer R.	Galv. Throw.	
73.990 cm.	12.60 cm.	23 Ω	2.8 mm.	18.64° C.
	12.64	22	4.9	
	12.59	23	2.3	
	12.60	22	5.0	
	12.57	23	2.8	
73.945	12.55	22	4.6	18.68°

Temp. oil 21.7° C. $\quad 24.21\ \Omega = R_0$

$\Delta p = 10.88$ gm./cm.^{2} $\quad 7384.3\ \Omega = R$ of Weston cell against storage

Errors Due to Inflow of Heat During Observation.—Both because the thermojunction has a finite heat capacity and because the expansion is oscillatory, it is necessary that the temperature should be measured at some definite time after the expansion is made. During this interval there is of course an inflow of heat which holds up the final temperature of the thermojunction. The effect of gas conduction and convection from the walls, which is present even in a 60 liter carboy, as shown by

Moody's work, is of course extreme in the 1 liter bulb; its magnitude, moreover, will vary in the present case with the way in which the thermo-junction is mounted in the bulb. There is also an inevitable transfer by radiation from the walls to the junction, and finally a possible inflow by metallic conduction. These errors are all proportional to ΔT, and vanish with it. It is consequently necessary that for a single thermo-junction, with a single interval between expansion and observation of temperature, sufficient data should be obtained to plot apparent values of γ as a function of Δp, or of the cooling. For expansions as small as those here employed (none are over 4 per cent.) this must be practically a linear function. Three different junctions, mounted in different tubes, were used in air with different metronome rates, and the data so plotted. Figs. 2 and 3 show that though the slopes differ widely, the intercepts are

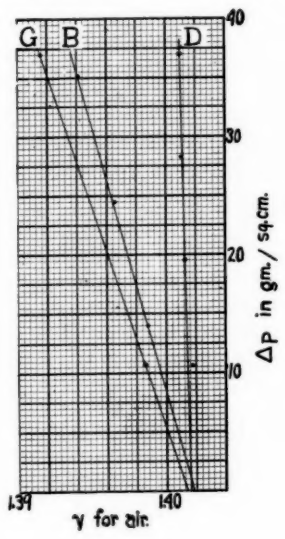

Fig. 2.

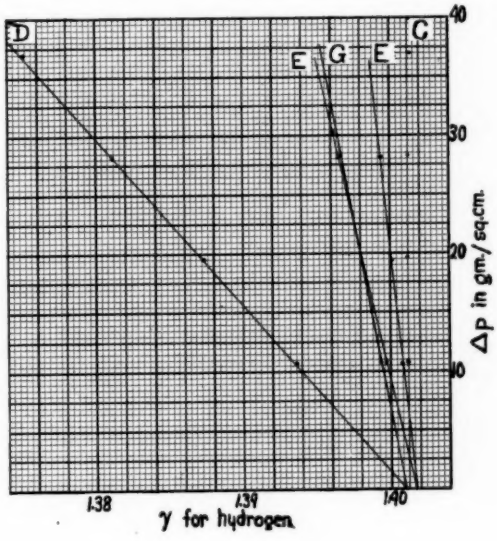

Fig. 3.

substantially the same. Two series of observations made with the same junction for $t = .75$ sec. and $t = .62$ sec. (see Table III., Junction E) indicate the extent to which the observed values depend upon the time of observation. Junction D was used with the same time interval in both air and hydrogen, and a comparison of the D lines in Figs. 2 and 3 shows how much more considerable the effect of heat inflow is in the case of hydrogen; this is partly due to the shorter time of expansion, and partly to the larger conductivity. It appears then that the data bear out satisfactorily the assertion that in the value of γ obtained by extrapolation for $\Delta p = 0$, the effect of inflow of heat by whatever means and

TABLE II.

Air.

	ΔP.	P.	T.	ΔT.	γ.	Mean γ.
Junction *B*, time, .87 sec.....	13.98 gm./cm.²	1,014.90 gm./cm.²	292.05°	1.133°	1.3971	
	14.00	1,007.50	292.04	1.138	1.3947	
	13.95	1,016.72	291.92	1.135	1.4000	
	14.21	1,012.46	291.20	1.156	1.3999	
	14.08	1,012.90	292.77	1.149	1.3985	
	14.01	1,011.56	292.71	1.151	1.4015	
	14.00	1,015.15	292.19	1.143	1.4010	
	14.05	1,014.82	292.18	1.140	1.3973	
	13.93	1,014.12	292.11	1.138	1.4007	
	13.91	1,019.70	291.83	1.121	1.3968	1.3988
	24.50	1,013.26	292.03	1.970	1.3953	
	24.51	1,008.00	292.02	1.986	1.3968	
	24.67	1,012.70	292.80	2.003	1.3990	
	24.49	1,011.98	292.08	1.967	1.3939	
	24.47	1,015.26	292.17	1.976	1.3985	
	24.46	1,014.00	292.13	1.969	1.3960	
	24.45	1,019.90	291.85	1.958	1.3971	
	24.46	1,018.90	292.01	1.960	1.3964	1.3966
	34.95	1,008.42	291.97	2.793	1.3929	
	35.12	1,012.68	292.79	2.812	1.3949	
	34.95	1,014.93	292.22	2.787	1.3949	
	35.00	1,012.13	292.04	2.811	1.3964	
	35.12	1,011.60	292.80	2.812	1.3943	
	35.04	1,012.86	292.66	2.805	1.3950	
	34.93	1,015.40	292.14	2.775	1.3932	
	35.02	1,019.30	291.96	2.760	1.3913	1.3942
Junction *D*, time, .87 sec.....	10.58	1,023.31	291.16	.857	1.4013	
	10.73	1,018.60	291.25	.872	1.4008	
	10.60	1,009.80	290.81	.871	1.4028	
	10.66	1,016.82	291.12	.869	1.4021	
	10.79	1,012.50	291.40	.885	1.4027	1.4019
	19.72	1,019.70	292.24	1.602	1.4024	
	19.43	1,010.30	290.79	1.597	1.4007	
	19.50	1,016.52	291.10	1.580	1.4015	
	19.66	1,016.15	291.37	1.600	1.4031	
	19.54	1,023.76	291.34	1.569	1.3998	
	19.61	1,011.50	291.46	1.596	1.4006	1.4013
	28.14	1,021.57	291.16	2.261	1.4023	
	28.38	1,021.30	292.30	2.268	1.3971	

TABLE II.—*Continued.*

	ΔP.	P.	T.	ΔT.	γ.	Mean γ.
Junction D, time, .87 sec.....	28.12 gm./cm.²	1,010.70 gm./cm.²	290.78°	2.284°	1.4032	
	28.24	1,016.56	291.14	2.277	1.4017	
	28.39	1,016.30	291.31	2.287	1.4008	1.4010
	37.11	1,020.50	292.26	2.981	1.4025	
	36.88	1,009.35	290.82	2.954	1.3988	
	37.03	1,016.42	291.26	2.972	1.4017	1.4010
Junction G, time, 1.0 sec.....	10.79	1,019.06	291.70	.874	1.3987	
	10.94	1,011.28	291.95	.892	1.3974	
	10.87	1,006.80	291.85	.894	1.4000	
	10.83	1,024.61	291.77	.874	1.3992	
	10.89	1,005.43	291.89	.894	1.3982	
	10.74	1,012.37	291.72	.878	1.4000	
	10.88	1,022.30	291.78	.878	1.3980	
	10.71	1,014.03	291.29	.869	1.3973	
	10.81	1,003.14	291.40	.888	1.3979	
	10.88	1,005.59	291.78	.895	1.3991	1.3986
	36.91	1,019.06	291.65	2.912	1.3929	
	37.13	1,010.07	291.90	2.945	1.3908	
	36.93	1,015.64	291.81	2.928	1.3935	
	37.13	1,013.47	291.85	2.936	1.3908	
	37.11	1,010.47	291.82	2.950	1.3921	
	37.01	1,023.96	291.40	2.890	1.3903	
	36.87	1,023.41	291.05	2.888	1.3922	
	36.81	1,017.17	291.90	2.888	1.3905	1.3916

Limiting values: $B = 1.4019$
$D = 1.4017$
$G = 1.4014$ Mean = *1.4017*

however extreme, unless the slope of the line is such as to make its intercept uncertain, is completely eliminated. Inasmuch as the errors inherent in the method are thus accounted for, it remains only to examine the observational errors.

Observational Errors.—The error in p_1, the barometric pressure read to .005 cm., would be inconsiderable were it not that a single observation requires at least an hour, and that in that time the barometer often changes by nearly a millimeter. For the smallest expansion a change of .5 mm. in p_1 is equivalent to a change in ΔT of .0003°. For this reason observations were always taken for alternately high and low points on the resistance-throw line.

Heights on the oil gauge were read to .01 cm. by means of a magnifying

TABLE III.

Hydrogen.

	ΔP.	P.	T.	ΔT.	γ.	Mean γ.
Junction C, time, .65 sec.....	10.85 gm./cm.²	999.51 gm./cm.²	291.72°	.901°	1.4017	
	10.52	1,023.78	290.24	.846	1.3997	
	10.67	1,022.72	291.68	.872	1.4037	
	10.85	1,022.70	292.90	.887	1.4003	
	10.67	1,008.67	291.45	.876	1.4006	
	10.63	1,007.63	291.52	.873	1.4003	
	10.70	1,016.74	291.26	.873	1.4022	
	10.74	1,025.44	291.32	.866	1.3999	1.4011
	19.60	999.95	291.57	1.612	1.3999	
	19.60	1,017.70	291.10	1.583	1.4004	
	19.59	1,011.94	292.86	1.598	1.3994	
	19.25	1,012.20	292.72	1.589	1.4061	
	19.55	1,019.30	292.03	1.588	1.4024	
	19.69	1,021.90	292.92	1.584	1.3970	
	19.49	1,010.90	291.22	1.589	1.4017	
	19.61	1,025.44	291.32	1.578	1.4019	1.4011
	28.36	1,019.30	292.08	2.273	1.3978	
	28.27	1,008.33	291.52	2.309	1.4037	
	28.40	1,018.74	292.47	2.306	1.4043	
	28.33	1,022.02	292.30	2.276	1.4004	
	28.41	1,019.03	292.92	2.301	1.4021	
	28.40	1,014.40	291.97	2.294	1.3999	
	28.36	1,027.36	291.94	2.267	1.4012	
	28.16	1,013.80	291.12	2.276	1.4015	1.4012
	36.94	1,000.75	291.66	3.003	1.3997	
	36.88	1,014.46	291.12	2.962	1.4013	
	37.03	1,015.40	292.54	2.988	1.4018	
	37.04	1,022.02	292.32	2.977	1.4035	
	37.14	1,019.03	292.69	2.986	1.4013	
	37.14	1,021.90	292.92	2.984	1.4021	
	36.89	1,014.80	291.09	2.967	1.4020	
	36.92	1,007.63	291.53	2.982	1.4000	1.4014
Junction D, time, .83 sec.....	10.79	1,013.00	291.51	.872	1.3924	
	10.74	1,000.90	291.12	.876	1.3934	
	10.62	997.24	290.62	.867	1.3902	
	10.70	1,008.95	290.92	.865	1.3929	
	10.72	1,015.20	290.62	.863	1.3963	
	10.44	1,011.80	290.35	.845	1.3962	
	10.71	1,006.35	290.77	.869	1.3941	1.3936

TABLE III.—*Continued.*

	ΔP.	P.	T.	ΔT.	γ.	Mean γ.
Junction D, time,						
.83 sec.....	19.61 gm./cm.²	1,003.85 gm./cm.²	291.72°	1.580°	1.3906	
	19.50	1,005.12	290.62	1.547	1.3847	
	19.61	1,016.85	290.72	1.549	1.3885	
	19.56	1,010.20	291.00	1.563	1.3900	
	19.39	1,010.45	290.40	1.523	1.3824	
	19.53	1,015.48	291.21	1.545	1.3874	1.3873
	28.28	1,003.80	291.72	2.255	1.3871	
	28.11	1,002.73	290.61	2.216	1 3830	
	28.29	1,016.45	290.70	2.190	1.3801	
	28.17	1,009.00	290.45	2.186	1.3780	
	28.19	1,006.35	290.77	2.198	1.3789	
	28.29	1,015.25	291.27	2.194	1.3792	1.3811
	37.01	1,003.75	291.77	2.869	1.3754	
	37.07	1,010.45	291.12	2.849	1.3758	
	36.98	1,015.60	290.62	2.830	1.3766	
	36.89	1,009.50	290.42	2.814	1.3725	1.3781
Junction E, time,						
.62 sec.....	10.75	1,021.50	291.60	.877	1.4038	
	10.76	1,010.68	292.22	.882	1.3993	
	10.51	1,037.40	290.78	.839	1.4011	
	10.56	1,036.70	290.42	.841	1.4007	
	10.64	1,016.90	290.59	.859	1.3977	
	10.67	986.90	291.23	.898	1.4028	1.4009
	19.58	1,021.70	291.68	1.577	1.3997	
	19.66	1,015.55	291.67	1.607	1.4047	
	19.29	1,039.70	290.02	1.515	1.3981	
	19.38	1,018.90	290.81	1.561	1.3998	
	19.46	1,011.75	291.03	1.575	1.3982	1.4001
	28.20	1,022.50	291.72	2.263	1.4010	
	28.06	1,036.90	290.87	2.216	1.4015	
	28.05	1,039.75	290.02	2.194	1.3990	
	28.17	1,015.00	291.16	2.252	1.3960	
	28.08	1,038.20	290.32	2.200	1.3986	1.3992
.75 sec.....	10.76	1,015.83	291.50	.877	1.4005	
	10.62	1,017.00	290.92	.861	1.3992	
	10.69	1,016.50	290.94	.867	1.3995	1.3997
	28.11	1,022.60	291.52	2.240	1.3975	
	28.04	1,035.40	290.92	2.201	1.3971	
	28.07	1,039.80	290.09	2.175	1.3938	
	28.10	1,038.40	290.32	2.190	1.3958	
	28.07	1,010.23	290.83	2.263	1.3986	1.3965

TABLE III.—*Concluded.*

	ΔP.	P.	T.	ΔT.	γ.	Mean γ.
Junction *G*, time, .65 sec.....	10.81 gm./cm.²	1,011.58 gm./cm.²	292.22°	.885°	1.3988	
	10.83	1,013.05	292.12	.885	1.3988	
	10.76	1,028.84	291.21	.866	1.4008	
	10.75	1,029.40	291.25	.862	1.3992	
	10.74	1,031.36	291.41	.859	1.3985	
	10.64	1,031.24	291.03	.849	1.3979	
	10.53	1,025.31	290.17	.847	1.4009	
	10.65	1,029.04	290.41	.850	1.3983	
	10.85	1,027.92	291.40	.873	1.3999	1.3992
	28.20	1,025.75	290.69	2.239	1.3987	
	28.34	1,028.56	291.17	2.238	1.3964	
	28.27	1,029.00	291.42	2.242	1.3984	
	28.15	1,030.82	291.36	2.225	1.3977	
	28.13	1,031.48	290.77	2.208	1.3947	
	28.02	1,024.90	290.21	2.215	1.3967	
	28.13	1,025.94	290.12	2.214	1.3950	
	28.30	1,026.30	291.40	2.236	1.3950	
	28.13	1,023.41	291.14	2.233	1.3966	1.3966

Limiting values: $C = 1.4012$
$D = 1.4011$
$E = 1.4016$
$G = 1.4011$ Mean = *1.4012*

glass and a small lamp to illuminate sharply the meniscus from beneath. A given pressure could be duplicated to about .05 cm. A temperature-density curve was obtained for the oil by the specific gravity bottle method which must be accurate to 1 part in 8,000. It is to be noted, however, that an error in the density of the oil, as also an error in the calibration of the thermojunction, these errors being proportional respectively to Δp and ΔT, do not appear in the final extrapolated value of γ at all. The maximum error in Δp may fairly be taken as .01 gm./cm.²; this corresponds to an error in γ of .0004 for the smallest expansion and .0001 for the largest.

The water bath, while it contained no thermostat, was large enough that the temperature was constant to less than .1° during an observation, the temperature being read to .01° on a mercury thermometer which had been calibrated against a Baudin standard thermometer. The uncertainty here introduced in γ is only .0001.

The major difficulty, of course, lies in the determination of ΔT. The galvanometer throws are so rapid, particularly in hydrogen, where the

conductivity is six times greater than in air, and the temperature change correspondingly rapid, that they cannot be read with precision. In each throw are involved the questions of the initial balance of the potentiometer, of the duplication of pressure, and the duplication of the time interval between opening the bulb and closing the potentiometer circuit. This last element of variation could be eliminated by the introduction of an automatic key, but in view of the other more considerable items this seemed unnecessary. The equilibrium resistance is determined from eight or ten throws, and may moreover be partially corrected if the mean slope of the line in question is already known from preceding observations. These resistances are probably obtained to the nearest .1 ohm, making a maximum uncertainty of .0006 and .0025 in γ for the largest and least coolings respectively.

The total possible error this accounted for in a single observation is larger than one would wish it. The actual mean deviation of observations in one group is, however, scarcely more than in Partington's data, and with a sufficient number of observations the slope of the γ-Δp line must be obtained with fair precision. It is also to be emphasized that several errors operate to modify the slope of the line without affecting the intercept, since for $\Delta p \doteq 0$, $\log(\theta_1/\theta_2) \doteq 0$ also. The worth of the work should therefore rather be judged by the variation in the intercepts. The three determinations for air and the five for hydrogen show a mean deviation in each instance of .0002; this may therefore fairly be taken to represent the probable error. (See summaries of Tables II. and III.)

Theoretical Correction.—The value of γ obtained from the ideal gas equation must be corrected in the case of air for departure from the ideal gas laws. The original Lummer and Pringsheim method was to compute the absolute temperature using $-272.4°$ C. as zero. This is numerically equivalent to the method used by Partington, who computes the correction from the Berthelot equation in the form,

$$\frac{1}{\gamma} = \frac{1}{\gamma i} - \frac{\frac{a}{v^2}\left(\frac{\theta_1}{(\theta_2)^2} - \frac{1}{\theta_1}\right)}{p_1 - p_2},$$

where γi is computed from equation (2), using $\theta = t + 273.09$. For the present purpose the limiting value of the correction term as $p_1/p_2 \doteq 1$ is required. This is readily found by substitution of $(p_1/p_2)^{(\gamma-1)/\gamma}$ for θ_1/θ_2, and differentiation to be

$$\frac{a}{pv^2\theta}\,\frac{\gamma - 1}{\gamma}.$$

Hence,

$$\frac{1}{\gamma} = \frac{1}{\gamma i}\left(1 - \frac{.4017a}{pv^2\theta}\right).$$

The mean values of the critical constants of air as determined by Olszewski and by Wroblewski give $a = .336$. It follows that for one atmosphere and 20° the correction factor is .99912 and the corrected value of γ is 1.4029. The correction for hydrogen is well beyond the limit of observation.

Discussion of Results.—The final values obtained from this investigation are for air 1.4029, and for hydrogen 1.4012.

Inasmuch as γ for air is already known with considerable certainty, the observations in air are to be regarded as a test of the precision obtainable in a small flask. A critical summary of the older work appears in Moody's paper, which points to the conclusion that neither the velocity of sound, nor the Clement and Des Ormes method, nor other direct application of Reech's theorem are capable of yielding as precise results as the Lummer and Pringsheim method. There are now three determinations by this method, as follows:

Lummer and Pringsheim	1.4025
Moody	1.4003[1]
Partington	1.4032

The close concordance between the present value and these which were obtained in large carboys, is a highly satisfactory vindication of the applicability of the method to small flasks. It is interesting to repeat in passing what others have called attention to, that, aside from the internal work, this high value for air is amply accounted for by its 1 per cent. argon content. Leduc's formula,[2] for example, gives 1.4015 for a mixture 99 per cent. of which has $\gamma = 1.400$ and 1 per cent. $\gamma = 1.67$.

The only available data for hydrogen are meager and conflicting. Oddly enough, only three attempts have been made to measure the ratio of the specific heats of hydrogen. Maneuvrier,[3] from direct application of Reech's theorem, gave for hydrogen 1.384, somewhat less than his value for air, 1.392, but he frankly states that he had not been able to secure the same consistency in hydrogen as in air. The exceedingly careful work of Lummer and Pringsheim, however, gave 1.4084 as compared with 1.4025 for air. Mercer in the same small flask found 1.398

[1] Moody's published value, 1.4011, has been increased by the theoretical correction .0012, pointed out by Partington, and it has been decreased by .0020, because the radiation error which he added had been already included, unmistakably it appears to the author, in the slope of his line.

[2] C. R., 160: 338, 1915.

[3] C. R., 123: 228, 1896.

for hydrogen and 1.392 for air. The work of Eucken on C_v and of Scheel and Heuse on C_p likewise give values of γ distinctly higher for hydrogen than for air (see Table IV.). The weight of existing evidence is therefore contrary to the present conclusion that γ for hydrogen is close to its theoretical value according to the kinetic theory. With the

TABLE IV.

	Observer.	γ.	c_p at 20° in 15° Cal.
a. Air.....			
	Regnault[1]	1.4008	.2408
	Lummer and Pringsheim	1.4025	.2400
	Swann[2]	1.3994	.2410
	Scheel and Heuse[3]	1.4013	.2408
	Moody	1.4003	.2409
	Partington	1.4034	.2396
	Shields	1.4029	.2399
b. Hydrogen.....			
	Lummer and Pringsheim	1.4084	3.400 (16°)
	Scheel and Heuse	1.4075	3.406 (16°)
	Shields	1.4012	3.443

[1] This is after correction by Scheel and Heuse, see Ann. d. Phys. 40: 486.

[2] Phil. Trans. Roy. Soc., 210: 199, 1909.

[3] Loc. cit. Scheel and Heuse's and also Swann's values are restated, using $J = 4.187$.

idea that the discrepancy might be explained if γ were a much more rapidly changing function of the temperature in hydrogen than it is known to be in air, in which case insufficient care had been exercised in controlling the temperature of the water bath, a series of observations were taken with the bulb in an ice bath. This series yielded 1.4006, however, and there appears no reason to discredit the data of Table III. on that score.

Comparison with Data on C_p.—Alongside these direct determinations of γ it is instructive to assemble once more the values of γ obtainable from observations on C_p. These latter may be computed in either of two ways: (*a*) from the relation $C_p - C_v = R$, corrected in accordance with a chosen equation of state, as was done by Scheel and Heuse and by Partington; (*b*) from the relation,

$$C_p = \frac{1}{J}\frac{\gamma}{\gamma - 1}\theta\alpha_p p_0 \alpha_v v_0,$$

employed by Moody, which is as universally rigorous as the thermodynamic theorems out of which alone it is derived, and all factors of which are known with extreme precision. The second method has been used in the computations herewith presented, the required constants being chosen as follows:

For air:

p = 13.595 × 980.616 × 76 (Landolt-Börnstein Tables).

θ_0 = 273.09, chosen by Berthelot as the thermodynamic temperature of melting ice (Zeit. für Elektrochemie, 10 : 621, 1904) and in agreement with the more recent work of Onnes, Richards, and Witkowski on the pressure and volume coefficients of hydrogen, and of Travers on helium.

α_v = .0036700, Chappuis' value reduced from 1,000 mm. to 760 mm. (Trav. et Mem. du Bur. Int. des Poids et Mes., 13: 190, 1903).

α_p = .0036713, likewise Chappuis' with the same reduction (loc. cit.).

J = 4.187 × 10^7 ergs per 15° cal. (Ames, Congres Int. d. Phys., 1: 178, 1900).

ρ_0 = .00129278, Regnault's value reduced to latitude 45°.

For hydrogen:

α_v = .00366256, Chappuis (loc. cit.).

α_p = .0036606, Chappuis, reduced to 760 mm.

ρ_0 = 8.9876 × 10^{-5}, the mean of Regnault's, Jolly's and Morley's values as quoted by Berthelot (loc. cit.).

The table gives observed values in Clarendon type, computed values in ordinary type.

In the case of air the computed values of c_p are, with the exception of Moody's, lower than the observed. This may be attributed to uncertainties in the data which are the basis of the computation; it is to be noted, however, that Partington's method yields values slightly lower yet. For hydrogen the two methods are identical, as would be expected when there is no question of equation of state.

II. At − 191° C.

The same one-liter flask was placed in a liquid air bath—an open metal can well packed in cotton so that two liters of air sufficed for one and a half hours' work—and it was found that observations could be obtained with surprising ease and precision. The fixed junction was kept in ice, and in order to balance the large electromotive force due to 190°, a second potentiometer was applied to the thermojunction circuit having a fall of 1.5 volts through about 800 ohms; 3 ohms were sufficient almost to balance the thermal E.M.F., and the close adjustment was made on the Wolff potentiometer arranged as before. In this way the resistance in the thermojunction circuit was kept small, and the thermometric arrangement was quite as sensitive as at 20°. It was more difficult to reproduce pressures, and the temperature of the bath inevitably changed by about .5° between beginning and end of a complete observation. The procedure was in other respects the same as at 20°.

The temperature-E.M.F. line was obtained very simply by measuring the E.M.F. in pure oxygen (used air was accumulated until a liquid was secured which maintained its temperature to 1/4000 for seven hours) and then in new air, the temperature of the latter being obtained from Baly's data[1] by displacing the line somewhat to accord with Henning's temperature for oxygen[2] (− 183.00°), and Fischer's for nitrogen[1] (− 195.67°) C. This method was checked closely by calibrating a platinum thermometer, and then calibrating the thermojunction against it. The calibration constant of the junction in this region is 1.68×10^{-5} volts per degree.

The data obtained are shown in Table V.

TABLE V.

ΔP.	P.	T.	ΔT.	γ.	Mean γ.
13.84 gm./cm.²	1,011.26 gm./cm.²	81.05° A.	.394°	1.559	
14.01	1,020.51	80.35	.394	1.564	
14.39	1,018.89	81.85	.411	1.561	
14.61	1,013.50	83.33	.427	1.560	
14.20	1,006.70	82.52	.419	1.571	1.563
36.79	1,020.80	81.50	.968	1.509	
36.82	1,018.89	82.43	.978	1.506	
37.11	1,006.35	82.30	1.015	1.521	
36.56	1,007.05	82.33	1.011	1.530	
36.43	1,012.90	82.51	1.011	1.535	1.520

γ for $P \doteq 0$, **1.590**

The correction factor for hydrogen at 82° Å. is 1.0011. Hence the final value in the ideal gas state is 1.592 at a mean temperature of 82°, as compared with Scheel and Heuse's value 1.595 at 92°, and Eucken's 1.605 at 92°, or 1.624 at 82°. (These latter are computed from the relation, $C_p - C_v = R$, corrected in accordance with Berthelot's equation, as indicated by Scheel and Heuse.) The value here obtained might be slightly smaller except for the unfortunate circumstance that the mean temperature of the bath during observations at $P = 14$ gm./cm.² is lower than at 37 gm./cm.². The smaller value of γ agrees more closely than Eucken's, however, with the Planck-Einstein formula for C_v. With a specially designed thermostat, this method might well be made a more precise method of investigating specific heats of gases at low temperatures than direct measurement of either C_p or C_v.

At the conclusion of this work the author wishes to testify to her

[1] Phil. Mag. (5), 49: 517.
[2] Ann. der Phy. (4), 35: 761.
[1] Ann. der Phy. (4), 9: 1149.

appreciation of the friendly interest of all the Ryerson staff during its progress, and to her especial indebtedness to Professor Millikan for the constant encouragement and helpfulness of his oversight.

SUMMARY.

1. Observations by the Lummer and Pringsheim method in a one liter flask have been found to yield for air, $\gamma = 1.4029$, a value in close agreement with already accepted values.

2. For hydrogen, γ is found to be 1.4012 at 18° C., 5. per cent. lower than previous values, with no apparent explanation of the divergence.

3. For hydrogen at $-$ 191° C., γ becomes 1.592, in general accordance with the quantum theory of specific heats.

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May, 1917.

NOTES ON MELDE'S EXPERIMENT.

By Arthur Taber Jones and Marion Eveline Phelps.

I. Vibration Form of Elements of the String.

Introduction.—Melde[1] studied the vibrations of a string of which one end was fixed and the other attached to one prong of a tuning fork. When the string was perpendicular to the axis of the fork and in the plane of its prongs he spoke of the system as being in the "parallel" position, and when the string was perpendicular to the plane of the prongs he spoke of it as being in the "transverse" position. In the cases of the simplest motions the frequency of the vibration which the fork imposes upon the string is equal to that of the fork for the transverse position and half that of the fork for the parallel position.

We have found that by using for the string a black fish cord in which white dots had been woven it is possible to see very clearly the paths of the separate elements of the string and even to obtain photographs of these paths.

The Parallel Position.—In this case if the end of the string which is not attached to the fork is fixed in position, the vibration of the fork produces a periodic change in the distance between the ends of the string. Thus the motion of each element of the string is compounded of a longitudinal component which has a frequency equal to that of the fork, and a transverse component which has a frequency twice that of the fork. The velocity with which a change of tension is propagated along the string is usually so great compared with the velocity with which transverse waves are propagated that we may regard the tension at any instant as being the same at all points of the string. In a system in which the damping is small the string passes through its equilibrium position when the tension of the string is greatest or least[2]—usually when it is greatest—so that the paths of the elements of the string are usually parts of parabolas with their convex sides turned toward the fork. Fig. 2 shows these parabolic arcs. The fork is at the right. It will be observed that the longitudinal component of the motion is practically constant from one end of the photograph to the other.

[1] Pogg. Ann., 109, p. 192, 1859; 111, p. 513, 1860.

[2] Rayleigh, Theory of Sound, ed. 2, Vol. 1, p. 84.

Raman[1] has shown that the string may be maintained in vibration with a frequency $m/2$ times that of the change in tension, where m is any integer. For $m = 1$ we have the case studied by Melde. Raman gives pictures of a string which is vibrating with two of these frequencies simultaneously, one of the two being always the frequency for which $m = 1$. The striking fact about Raman's cases is that the string vibrates in one loop for both frequencies.

Fig. 3 shows a case in which the frequency of the string equals that of the fork. This frequency ratio is shown by the fact that the paths are nearly straight lines. Thus these lines make immediately evident what Raman has deduced[2] with the aid of his Fig. 7.

Fig. 4 shows a case in which the string is vibrating simultaneously with two loops and with five, but in which the frequencies are not in the ratio of two to five. A node for the form with two loops is near the middle of the photograph, and nodes for the form with five loops are a little beyond the ends of the photograph. The frequency of the vibration with two loops is half that of the fork, as is seen from the fact that near the ends of the photograph the curves approach arcs of parabolas. The frequency of the vibration with five loops is three halves that of the fork, as is seen from the fact that the curves in the photograph have in general the forms shown in Fig. 1. a is the form toward the left of the photograph, b near the middle, and c toward the right. These curves are drawn from the equations

Fig. 1.

$$\text{for all curves} \quad x = -1.25 \cos 2pt,$$

$$\text{for } a \quad y = 3 \cos pt + 3 \cos 3pt,$$

$$\text{for } b \quad y = 3 \cos 3pt,$$

$$\text{for } c \quad y = -4 \cos pt + 2 \cos 3pt.$$

For Fig. 4 the string was about 70 cm. long, of linear density about 2.2 mg./cm., and was driven by a fork of frequency 100 vd. The tension could be varied by turning a screw eye, around which the fixed end of the string was wrapped. When the photograph was taken the string was vibrating in a plane, but it is quite as easy to obtain this figure when the string shows two loops in one plane and five in a perpendicular plane.

[1] PHYS. REV., 35, p. 453, 1912.

FIG. 2.

FIG. 3.

FIG. 4.

FIG. 5.

FIG. 6.

A. T. JONES AND M. E. PHELPS.

We have here then a case similar to those studied by Raman, in that the string is simultaneously executing vibrations with two frequencies which are not proportional to their respective numbers of loops. This seems to mean that *two transverse disturbances are simultaneously propagated along one string with different velocities.*

The Transverse Position.—In this position the frequency of the string is the same as that of the fork. For certain tensions the paths of the elements of the string may become circles, in planes perpendicular to the length of the string. Figs. 5 and 6 show the string when vibrating in this manner. For Fig. 5 the camera was placed at an oblique angle to the string, so that only the part near the middle of the photograph was well focused. For Fig. 6 the camera was perpendicular to the string. At the extreme ends of Fig. 6 the circles begin to show as very narrow ellipses.

The explanation of these circles appears to involve a force of double frequency. Consider the system in the transverse position and the string vibrating in a plane. When the string is in either of its extreme positions its length—and therefore its tension—is greater than when it passes through its equilibrium position. Thus the tension of the string is subject to a periodic change of which the frequency is twice that of the vibration of the string. This periodic change of tension can maintain a transverse vibration of the string with a frequency[1] which is the same as that with which the string is already vibrating. For brevity we will call the vibration which is immediately due to the motion of the fork the "motional" vibration, and that which is due to the change in tension the "tensional" vibration.

When the damping is small the tensional vibration will pass through its equilibrium position when the tension is greatest or least[2]—usually when it is greatest. Thus the tensional vibration will either be in phase with the motional vibration or will differ from it in phase by 90°—usually the latter. If the phases are the same, or if the planes of vibration happen to be the same, the two motions compound into a plane motion. But if the phases differ by 90°, and the vibrations happen to lie in perpendicular planes and to have equal amplitudes, the resultant motion will be circular.

Now for the motional vibration the end of the string which is attached to the fork does not lie quite at a node, whereas for the tensional vibration it does. Thus the distance between nodes is slightly different for the two motions. The result is that near the nodes the circles pass over into

[1] Rayleigh, Theory of Sound, ed. 2, § 68*b*.

[2] Rayleigh, Theory of Sound, ed. 2, Vol. 1, p. 84.

ellipses—with major axes approximately parallel to the motion of the prong on one side of the node and perpendicular to it on the other. These ellipses are easily observed.

It may be thought that the change of tension produced by the change in length of the string during vibration would not be sufficient to maintain a vibration of sufficient amplitude to produce the above effect. But the length of one wave of a string which has the form of a sine curve of wave-length 50 cm. and amplitude 1 cm. is about 2 mm. greater than its horizontal projection, so that the increase in tension would in this case be the same as that due to an amplitude of a millimeter in the prong of a fork in the parallel position. It is also to be remembered that the force which produces the motional vibration is applied farther from a node than that which causes the tensional vibration.

II. ROTATION OF THE PULLEY.

J. S. Stokes[1] observed that when the Melde apparatus is in the parallel position and the string passes over a pulley, the pulley may sometimes be set into a more or less steady rotation. Raman and Apparao[2] have also observed a rotation of the pulley. When the string passes horizontally from the fork to the pulley and then downward we will call a rotation in which the top of the pulley moves toward the fork a *rotation toward* the fork, and a rotation in which the top of the pulley moves away from the fork a *rotation away* from the fork. Stokes found that when the pulley was rotating toward the fork, waxing the string near the pulley led to rotation away from the fork, and cutting off the wax with oil restored the rotation toward the fork.

Shortly afterward one of us found that if the string passed through a small hole placed at the node nearest to the pulley, a rotation toward the fork could sometimes be produced by moving the hole a short distance toward the pulley, and a rotation away from the fork by moving the hole a short distance away from the pulley. Thus the pulley turned away from the fork when the segment which ended at the pulley was longer than it would be for the free vibration of the string, and toward it when the segment was shorter. We have checked this result by calculating the lengths of the loops of the free vibration for different loads, and then applying several loads which were in the neighborhood of those calculated. For the smaller of these loads the rotation is in general away from the fork and for the larger toward it.

It had seemed possible that the change in the sense of rotation observed

[1] PHYS. REV., 30, p. 659, 1910.

[2] PHYS. REV., 32, p. 307, 1911.

by Stokes might be due to a stiffening of the string by the wax and a consequent change in the distance between the nodes of the free vibration, but if that were the explanation his rotations would apparently not have been in the senses he observed.

For short strings it is difficult, if not impossible, to obtain rotation away from the fork, whereas rotation toward the fork is usually easy to obtain. Sometimes the rotation is very slow and sometimes the pulley makes several turns in a second. Frequently the sense of rotation may be changed by simply changing the amplitude with which the fork is vibrating, a small amplitude giving rotation away from the fork and a large amplitude rotation toward it. Rotation away from the fork appears to occur only when any motion that the string may have is pretty steady, whereas much irregularity in the vibration of the string is almost sure to cause an irregular turning of the pulley toward the fork. Moreover a rotation of the pulley in either sense may be obtained when the string is not, at least visibly, executing any transverse vibration at all.

When the string vibrates transversely this transverse motion may in certain cases be just sufficient to take up the slack given by the approach of the prong, so that no vibration or change of tension is transmitted to the pulley or beyond it. In a case which appeared to be of this sort we have measured roughly the amplitude of the motion of the string, assumed the string to be displaced in a sine curve, and have found that the length of this sine curve really did exceed its horizontal projection by an amount which checked, within the limits of experimental error, with the double amplitude of the tuning fork—in this case 7 mm.

The rotation of the pulley is doubtless due to an intermittent slipping of the string along the pulley at a phase of the vibration at which the friction between them is too small to supply the acceleration which would be necessary to prevent the slipping. A beginning has been made at the theory of the rotation, and that together with further experimental work will form the subject of another paper.

SMITH COLLEGE,
June 19, 1917.

THEORETICAL CONSIDERATIONS CONCERNING IONIZATION AND SINGLE-LINED SPECTRA.

BY H. J. VAN DER BIJL.

IN the following an attempt is made to give an explanation of some of the rather conflicting results on the ionization and characteristic radiation produced by the passage of electrons through gases and vapors. Most of the investigations of these phenomena were performed with mercury vapor, but the following considerations will in the main apply also to other monatomic gases and vapors.

The most important result of the experiments of Franck and Hertz[1] is that collisions of electrons with molecules of mercury vapor are elastic until the electrons have acquired energy equivalent to 4.9 volts. After having dropped through this voltage the electrons lose all their energy on collision and at the same time energy is radiated. This radiated energy Franck and Hertz identified as the single-line 2536 Å.U. This shows that the mercury atom does not take any energy from the colliding electron unless the latter has a definite minimum amount of energy to give to the atom. Furthermore, in view of the fact that, according to the Planck-Einstein relation $Ve = h\nu$, the frequency of the line 2536 corresponds to 4.9 volts, the experiments of Franck and Hertz gave evidence in favor of the quantum theory. They concluded from their experiments that when the electrons have dropped through 4.9 volts, ionization of the mercury vapor sets in. By using Lenard's[2] method of picking out the positive ions, they actually observed what appeared to be ionization at 4.9 volts. This result was later confirmed by McLennan and Henderson,[3] Goucher[4] and others. McLennan and Henderson also found that the single line 2536 was emitted when the atoms of mercury vapor were bombarded by 4.9 volt electrons, and established a similar result for cadmium and zinc.

These results presented two difficulties: Firstly, although the result that the collision of an electron with an atom of a monatomic gas is elastic when the electron collides with energy less than a certain definite

[1] Verh. d. D. Phys. Ges., 16, 457 and 512, 1914.
[2] Ann. d. Phys., 8, 149, 1902.
[3] Proc. Roy. Soc., A, 91, 485, 1915.
[4] PHYS. REV., 8, 561, 1916.

amount is in conformity with the quantum theory, such conformity does not exist if ionization as well as radiation is produced by the transference of this definite amount of energy from the colliding electron to the atom. Secondly, the quantum theory requires that the transference of this amount of energy should give rise to the stimulation of a single line. But if, on the other hand, a stream of colliding electrons is used (as is always done) the emission of a single line is not compatible with Bohr's theory of the atom. It is because of these definite and important questions that experiments along these lines may reasonably be expected to furnish valuable evidence regarding the validity of the quantum hypothesis and particularly Bohr's theory of atomic structure.

As regards the first question, viz., the production of ionization simultaneously with the stimulation of the 2536 line in mercury, I pointed out that the ionization effect observed at 4.9 volts may, under certain conditions, not be impact ionization, but a photoelectric effect[1]: The stimulation of the line 2536 establishes a source of ultraviolet light in the discharge tube and so causes a dislodgment of electrons with the attending phenomena of ionization. On this view, what we might call the ionization voltage of mercury vapor would be 10.4 instead of 4.9 volts. This view has since been confirmed experimentally by Goucher.[2]

As regards the second question, the reality of the single-lined spectrum does not seem to have been established. McLennan[3] found that the many-lined spectrum was not produced until the colliding electrons have acquired an amount of energy equivalent to about 10 volts, this voltage, according to the quantum relation, corresponding to the line 1188 Å.U., which is the limiting line of the series of which 2536 is the first member. This result they also found with the vapors of cadmium, zinc and magnesium. On the other hand, Hebb and Millikan[4] find that the mercury arc, emitting its many-lined spectrum, can be made to strike with any voltage greater than 4.9 volts. I have been informed that at the April meeting of the Physical Society McLennan reported that by using dense electron streams as suggested to him by Millikan he had confirmed the latter's results.

In discussing this matter at the New York meeting of the Physical Society last December I pointed out that the apparent discrepancy could be explained away on the basis of the quantum hypothesis of atomic radiation by considering three factors:

[1] Proc. Am. Phys. Soc., Chicago meeting, Dec. 1, 1916. I wish to point out here that since the publication of this suggestion I found that Bohr had himself suggested the possibility of a photoelectric effect to explain the apparent discrepancy between the observed ionization voltage and that calculated from his theory of atomic structure.

[2] Read at February meeting of Am. Phys. Soc., 1917. PHYS. REV., 10, 101, 1917.

[3] Proc. Roy. Soc., A, 92, 305, 1916. [4] PHYS. REV., 9, 371 and 378, 1917.

1. As soon as the gas or vapor is brought into a state of excitation the size of the atoms increases, with a resulting transformation of the atomic system into one of higher potential energy.

2. When the colliding electrons have acquired sufficient energy to displace electrons from the outermost orbit, the radiation, resulting when the displaced electrons drop back to any configuration corresponding to one of lower potential energy than that which the system has acquired by virtue of the collision, stimulates a photoelectric effect with the resulting production of dislodged electrons.

3. The apparent distribution of velocities of the colliding electrons may, under certain circumstances, produce an appreciable influence.

Let us consider these influences in succession and see in how far they are capable of lending an explanation of the observed phenomena.

1. That the atomic diameter must increase with the excitation of the gas or vapor is in strict accordance with the quantum hypothesis, and in fact, follows as a natural consequence of it. This is easily seen by considering the simplest case, namely that of hydrogen. This atom has only one electron and one positive nucleus, the electron being in the orbit corresponding to the minimum potential energy of the system. We shall call this orbit 1. Now the Balmer series is stimulated by the displacement from (and consequent dropping back to) the orbit 2; the Paschen series by the displacement from the orbit 3. Only the Lyman series is stimulated by a displacement from the first orbit. Thus, if the electron is displaced from 2 to 3 and drops back to 2 we obtain the first line of the Balmer series; 2 to 4 gives the second line of the Balmer series and so on. It is therefore evident that *in the state of excitation of the gas* there must be many orbits outside the first which contain electrons, some atoms having, at any particular moment, electrons in the first orbit, others having their electrons in the second, others in the third orbit, and so on.

It is easily seen what is the cause of this increase in the potential energy of the whole system. If there are only a few colliding electrons the chance of this happening would be very small. But if a dense stream of electrons is used, then a bound electron which has been displaced by a colliding electron to an orbit corresponding to higher potential energy stands a good chance of being knocked out again by another colliding electron before it has had a chance to drop back to its original orbit and so will emit a line which belongs to an entirely different series from that to which belongs the line it would have emitted if it had had a chance to return to its original orbit. Thus, if the electron of a hydrogen atom is displaced from orbit 1 to orbit 3, it would, if it could return

to 1, emit the second line of the Lyman series; if, however, it is displaced again by another electron before getting a chance to drop further back than orbit 2, it would emit the first line of the Balmer series.

The same holds true for mercury. It follows from the experiments of Franck and Hertz that the most loosely bound electrons in the mercury atom in the normal state of its vapor are those which require a minimum amount of energy equivalent to 4.9 volts (2536 Å.U.) to displace them from their position of equilibrium. In the light of the Bohr theory this would mean the outermost stable orbit which contains electrons in the normal state of the vapor is that which corresponds to a potential energy equivalent to 4.9 volts less than the next succeeding orbit (reckoned from the center of the atom outwards) and which requires 10.4 volts to completely detach an electron from it. Now, as a matter of fact, the mercury spectrum shows many lines of much greater wave-length than this ultra-violet line 2536. These lines must be stimulated by displacements through orbits of greater potential energy than that corresponding to 2536. In other words, a smaller amount of energy than 4.9 volts is required to stimulate them, although the experiments of Franck and Hertz show that the smallest amount of energy that can cause any stimulation at all is equivalent to 4.9 volts. This all means that if the frequency of collisions of the impacting electrons with the atom is small, the line 2536 will be radiated when the colliding electrons have dropped through 4.9 volts. But if a dense stream of electrons is used some of the bound electrons that have been displaced from the outermost orbit which in the normal state of the vapor contains electrons (say orbit n) to the next succeeding orbit ($n + 1$), will be displaced again by other colliding electrons before getting a chance to drop back to their original orbit n, and some of these may be displaced from $n + 2$ before dropping back to $n + 1$, and so on. Hence, if we got an instantaneous picture of the vapor when bombarded by a dense stream of electrons, we would see atoms of various sizes, some being several times larger than the atoms in the normal state of the vapor.

Now, the energy necessary to displace an electron from the orbit $n + 1$ to $n + 2$ is much less than that necessary to cause a displacement from n to $n + 1$, the energy decreasing with the number of the orbit. This follows from Kossel's[1] frequency relations:

$$\nu_{\beta_n} = \nu_{a_n} + \nu_{a_{n+1}},$$

$$\nu_{a_n} = \nu_{a_n} + \nu_{a_{n+1}} + \nu_{a_{n+2}} = \nu_{a_n} + \nu_{\beta_{n+1}},$$

$$\cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots$$

$$\cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots$$

$$\nu_{\infty_n} = \nu_{a_n} + \nu_{\infty_{n+1}},$$

[1] Verh. d. D. Phys. Ges., 16, 953, 1914.

where α, β, etc., represent the number of the lines in the several series and n and $n + 1$, etc., the different series corresponding to the successive stable orbits n, $n + 1$, etc. For the K-series of characteristic X radiations, according to Kossel, $n = 1$, the series thus resulting from displacements from the innermost orbit; for the L-series, $n = 2$, etc. It is interesting to note that a displacement even from the outermost orbit which in the normal state contains electrons, does not, for the elements investigated, give rise to visible radiations; the lowest frequencies that the normal mercury vapor atom, for example, can give are the ultra-violet series $2536 \cdots 1188$. According to these views the Lyman series of hydrogen are nothing else than Barkla's K-series of characteristic X-radiations for hydrogen; the Balmer series the L-series of Barkla.[1]

The above frequency relations are general and have been tested by Kossel for X-radiations and recently by Millikan[2] for ultra-violet radiation from mercury vapor. Kossel deduced these relations from general considerations of the manner in which energy transformations are supposed to take place in the Bohr atom. But they also follow directly from Bohr's equation:

$$\nu = N\left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2}\right),$$

of which a number of spectral series have been found to be special cases. According to this equation ν_{α_n} is given by

$$\nu_{\alpha_n} = N\left(\frac{1}{n^2} - \frac{1}{(n+1)^2}\right).$$

Similarly,

$$\nu_{\beta_n} = N\left(\frac{1}{n^2} - \frac{1}{(n+2)^2}\right),$$

$$\nu_{\alpha_{n+1}} = N\left(\frac{1}{(n+1)^2} - \frac{1}{(n+2)^2}\right).$$

Hence,

$$\nu_{\alpha_n} + \nu_{\alpha_{n+1}} = N\left(\frac{1}{n^2} - \frac{1}{(n+2)^2}\right)$$

$$= \nu_{\beta_n},$$

which is Kossel's relation.

From the above consideration of the increase in atomic diameter it follows that one would not expect to obtain a single-line spectrum unless the stream of colliding electrons is very attenuated. In such case the

[1] Other strong evidence for this conclusion is presented in Millikan's recent presidential address to the American Physical Society.

[2] Loc. cit., p. 378.

lines of longer wave-length will be so weak that they will not show on the photographic plate. As the density of the stream of electrons is increased the intensity of the long wave-length lines will increase. If the electron stream is very dense, as in the case of the mercury arc, the long wave-length lines will become very intense. Furthermore, on account of the increase in potential energy when the atom "swells" the energy required to completely detach an electron from the atom becomes less than 10.4 volts. In fact, from Kossel's relation it is seen that the necessary amount of energy for this may be as low as 4.9 volts and even less. And hence ionization by successive impacts may take place even at these low voltages. In general the ionization at these low voltages may not be great, but in the case of a dense stream of electrons as in the mercury arc, it may be considerable.

2. The second point to be considered is the photoelectric effect due to the light radiated from the atoms in their attempt to regain their original configuration after having been disturbed by the impacting electrons. In the case of devices like Lenard's, in which a third electrode in the form of a screen is interposed between cathode and plate, most of the effective excitation, when the applied voltage is about 5 volts, takes place between the screen and the plate. It is therefore to be expected that a great part of the photoelectric effect would act on the plate. The positive ions formed by collision ionization would not have an appreciable influence on the distribution of potential between the cathode and the screen, because they are drawn to the plate, which, it will be remembered, is always maintained at a negative potential with respect to the cathode. In the case of a two-electrode device the photoelectric effect on the plate, which is now anode, will not have any influence, since the photoelectrons cannot come out of the positive plate, or will at least be returned to the plate when they do come out. The photoelectric effect can, however, also manifest itself by its action on the neighboring atoms and, as we shall see below, also on the cathode. Millikan has recently applied the photoelectric effect produced by the line 2536 on the neighboring atoms to explain the appearance of the lines of longer wave-length than 2536 on his photographic plates, on the basis that the observed photoelectric long wave-length limit of mercury is 2800 Å.U. He has pointed out, however, that so far as his argument is concerned it is immaterial whether the photoelectrically liberated electrons come from the mercury vapor, from condensed films of mercury or from the substance of the cathode, and he accordingly leaves the question of their origin entirely open, insisting only on their being produced photoelectrically. With respect to this question, it must be remembered that the photoelectric effect

will exert an influence in producing positive ions from the atoms at low voltages only in virtue of the swelling of the atoms when the vapor is brought into a state of excitation. As stated above, it follows directly from the experiments of Franck and Hertz that the normal mercury vapor atom does not generally contain electrons in orbits greater than that corresponding to the series 2536···1188, and hence, if there were no swelling, that is, no increase in potential energy by successive impacts by electrons or successive stimulation by light, the least amount of energy that could stimulate any radiation from that atom would be that which is equivalent to 4.9 volts. And therefore the photoelectric effect due to the stimulation of the line 2536 by an atom could only cause the absorption and reëmission of this line by another atom, and would not assist in the direct multiplication of positive ions.

The emission of electrons from atoms of the vapor cannot be determined by the photoelectric long wave-length limit of the substance itself. This quantity is a different thing from the long wave-length limit of the photoelectric effect on the atoms in the gaseous state of the substance. In the latter case this quantity is determined by the energy necessary to completely detach an electron from the atom, whereas in the former case the energy necessary to detach an electron from the atom must be very small because of the frequent collisions of the atoms in the solid state of the substance and the effect of the electrons in the neighboring atoms, and therefore the photoelectric long wave-length limit of the solid or liquid is mainly determined by the work which an electron must do in order to escape from the surface of the substance. The following table shows the difference between these two quantities for a few substances. The long wave-length limits of the solids and of the atoms in the gaseous state of the substance respectively are denoted by λ_0 and λ_c, and the equivalent voltages by V_0 and V_c. The values of V_0 are taken from photoelectric and thermionic measurements, while the values of V_c are calculated from the convergence wave-lengths λ_c of the principal series, and are assumed, for reasons developed in this paper, to represent the ionization voltages of the substances.

Substance.	λ_0.	λ_c.	V_0.	V_c.	$V_c - V_0$.
Mercury....	2800 (Millikan)	1188 (Paschen)	4.44	10.4	6.0
Zinc.....	3570 (Richardson)	1320 (Paschen)	3.48	9.24	5.8
Magnesium .	3750 (Richardson)	1336 (Paschen)	3.32	9.13	5.8
Calcium	3660	1246 (Lyman)	3.4 (W. Wilson)	9.96	6.6

The data available at present are far too meager to warrant any importance being attached to the fact that the difference between V_0 and

V_c for the substances given here is nearly constant. If, however, this were to be found to be generally true, it would mean that if the ionization voltage of a substance is less than about 6 volts, or if the substance has a convergence wave-length of the principal series greater than about 2000 Å.U., it should be photoelectrically active in the dark.

The values given in the table show, at any rate, that there is a considerable difference between the energy necessary to detach an electron from the solid or liquid and that required to detach an electron from an atom in the gaseous state of the substance. Since, therefore, the long wave-length limit of the mercury atom in the gaseous state is 1188 Å.U. the line 2536 cannot detach electrons from the normal mercury atom. All the atom can do is to absorb the light and may reëmit it. But in absorbing it the potential energy of the electron in the atom is increased, and if it is again exposed to 2536 radiation before getting a chance to reëmit the absorbed light its potential energy will be further increased, and by a third stage of the process the electron will be knocked out of reach of the attracting forces of the atom and will be carried away by the applied electric field. Also, as explained above, the transformation of the atom into a configuration of higher potential energy will give rise to the emission of light of different wave-length from the line 2536.

The great difference between the photoelectric long wave-length limit of a substance and that of the atoms of its vapor carry weight in the explanation of the maintenance of an arc, say between mercury and iron electrodes. It means that since a great deal of the light emitted by the stimulated atoms is of shorter wave-length, and therefore of greater energy, than the minimum amount of energy necessary to liberate electrons from the surface of the substance, there must be a copious emission of electrons from the cathode under the influence of the light radiated by the atoms, and these electrons must on account of the difference between V_0 and V_c be emitted with appreciable velocity. Thus, if they are liberated by the convergence line 1188 they will start with an initial velocity of about 6 volts; those that are liberated by the intense line 2536 will have an initial velocity of about 0.4 volt.

3. This brings out the importance of the initial velocities, even in the case in which a hot filament is used as cathode, and where the arc is seldom very intense. There is no reason why an appreciable number of electrons should not be emitted by the hot cathode photoelectrically once the gas or vapor is stimulated. If, for example, a calcium-coated platinum cathode is used the line 2536 would liberate electrons from it with an initial velocity of 1.5 volts. Adding these electrons to those that are emitted thermionically with Maxwellian velocities, we see that

the initial velocities can under certain circumstances have quite an appreciable influence in maintaining an arc at applied voltages less than that necessary to ionize the atom, and in fact less than that necessary to cause any stimulation at all of the normal atom.

It is possible that the comparatively high velocities with which electrons may be emitted from the cathode under the influence of the light from the stimulated atoms may account for the discrepancy in the experimental results on the ionization of helium. Franck and Hertz,[1] Pawlow[2] and Bazzoni[3] find the ionization voltage of helium to be about 20 volts, while Bohr's theory requires that it should be 29 volts. Bazzoni took special care to purify his helium and used a device which consisted only of a hot-wire cathode of tungsten and a cylindrical anode. His current-voltage curves show a very sharp increase at about 20 volts, thus indicating the occurrence of impact ionization. While it is true that there could not have been any photoelectric liberation of electrons from the anode in his device, it is quite possible that there might have been such electron liberation from the tungsten cathode. Remembering that the photoelectric long wave-length limit of tungsten, according to thermionic measurements of Langmuir, is equivalent to 4.5 volts, it is seen that 20-volt light, which has a wave-length of only 620 Å.U., should be capable of liberating electrons from tungsten with the high initial velocity of about 15 volts, so that when the applied voltage is 20 the energy of these electrons, on reaching the anode, would correspond to about 35 volts. The current would therefore not only be increased by the extra electrons liberated photoelectrically from the cathode, but also by the electrons dislodged from the helium atoms by these high velocity electrons. Adding to this effect the increase in potential energy by successive impacts, as explained above, we see that quite a considerable amount of ionization can take place under an applied voltage which is too low to ionize the normal helium atom.

The fact that ionization does not set in until the applied voltage is 20 volts gives, when we consider the effects that manifest themselves here, a rather striking confirmation of Bohr's theory, because it follows from his theory that this is just the voltage necessary to displace an electron from the orbit, which in the normal state contains the two electrons, to the next succeeding orbit. According to the theory of Bohr the energy radiated in the formation of single orbit atoms is given by

$$W = W_0 \Sigma F^2,$$

[1] Verh. d. D. Phys. Ges., p. 34, 1914.
[2] Proc. Roy. Soc., 90, 398, 1914.
[3] Phil. Mag., 32, 566, 1916.

where W_0 is the ionization energy of the hydrogen atom and F is given by

$$F = N - \frac{1}{4}\sum_{s=1}^{s=n-1} \operatorname{cosec} \pi \frac{s}{n},$$

N being the number of nuclear charges and n the number of electrons in the orbit. Since for helium $N = 2$ and $n = 2$, this gives for the formation of the helium atom an energy dissipation equivalent to 6.12 W_0 and for the binding of only one electron with the double nucleus, 4 W_0. Hence the ionization energy of helium is $(6.12 - 4)W_0 = 2.12\ W_0$ and the energy necessary to displace an electron to the next stable orbit

$$2.12 W_0 \left(1 - \frac{1}{4}\right).$$

Since W_0 is 2.16×10^{-11}, this gives 21 volts. It is therefore to be expected that ionization in helium should start at about 20 volts, because this is the minimum voltage necessary to cause the swelling of the atoms and the liberation of the photoelectrons.

It is seen, therefore, that a consideration of the three factors: the increase in atomic potential energy by successive impacts, the photoelectric effect of the light emitted by the stimulated atoms and the initial velocities of the electrons emitted from the cathode affords an explanation of the results obtained by workers in this field. In particular, the recently published results of experiments of Millikan and Hebb are just what is to be expected from these considerations. The fact that Franck and Hertz and McLennan obtain single-line spectra is due, as Millikan also pointed out, to their probably not having used dense electron streams.

It is now evident that the quantity which can be called the ionization voltage of a gas or vapor is not necessarily the minimum voltage required to ionize the gas or vapor. This latter voltage, we have seen, depends more on extraneous conditions than on the nature of the substance, and can therefore not be considered a property of the substance. According to the views postulated above ionization voltage must be defined as the equivalent of the minimum energy necessary to completely detach an electron from the *normal atom*, and is therefore the least voltage through which one electron must drop to ionize the normal atom. This quantity is a property of the substance only and does not depend on extraneous influences. It is determined by the equation

$$V = \frac{h\nu_e}{e},$$

where ν_e is the convergence frequency of the principal series, h is Planck's constant and e the elementary charge.

In view of the disturbing influences discussed above it would seem that the experimental determination of the ionization voltage is not a simple matter. The observed ionization at voltages below that required by the Bohr theory does not necessarily invalidate this theory. On the contrary, the fact that ionization is observed to start at the voltages necessary to cause the minimum displacement of an electron from the outermost orbit of the normal atom, seems, on the basis of the interpretation given here, to lend support to the Bohr theory.

RESEARCH LABORATORY, WESTERN ELECTRIC CO.,
NEW YORK,
May 30, 1917.

THE PARALLEL JET HIGH VACUUM PUMP

BY WILLIAM W. CRAWFORD.

EFFORTS to make a vapor aspirator-ejector produce a high vacuum have met the difficulty that the jet, when surrounded by a high vacuum, disperses and refuses to entrain the gas. Gaede[1] overcame this difficulty by confining the vapor stream in a practically continuous wall, through a narrow slit in which the gas enters the vapor stream. Williams[2] constricts the stream at the point of entrainment, causing it to pass this point with an increased velocity and reduced pressure, and finds that the narrow slit can be practically dispensed with. He provides a water-cooled surface at the point of entrainment to condense the vapor which tends to pass into the vacuum space. Langmuir[3] investigated the conditions in this type of pump more thoroughly, and reached the conclusion that the cooled surface is the essential element; the constriction of the stream does not appear in Langmuir's pump. Langmuir holds the view that a jet necessarily must disperse in a vacuum, and utilizes the dispersing vapor (apparently the major portion of the jet) to urge the gas along a surface on which the vapor condenses, and into the remainder of the jet, which delivers the gas to the rough pump.

According to the kinetic theory of gases, the paths of molecules between collisions are substantially rectilinear. At very low pressures, these paths become limited only by the walls of the chamber.[4] If the molecules emanate from a point and condense upon the walls, the linear path becomes evident from the location of shadow patterns of obstacles in the chamber.[5] Wood[6] has shown by this method that a mercury jet may be produced which does not disperse materially in a high vacuum.

If the molecules in Wood's jet retain variegated velocities, it seems clear that the limiting density for the jet cannot be much higher than that for Knudsen's molecular flow, since the faster and slower molecules

[1] Annalen der Physik, 1915, p. 357.

[2] PHYS. REV., May, 1916, p. 583.

[3] PHYS. REV., July, 1916, p. 48, Jour. Frankl. Inst., Dec., 1916, General Electric Review, Dec., 1916. See also Knipp, PHYS. REV., April, 1917, p. 311, and Jones and Russell, PHYS. REV., Sept., 1917, p. 301.

[4] Knudsen, Ann. d. Phys., 4, 28, 1909, p. 75.

[5] Anthony, Trans. A. I. E. E., 11, 133, 1894.

[6] Phil. Mag., Aug., 1915.

would have to traverse the entire length of the jet without colliding with molecules which they are overtaking, or being overtaken by. Such a jet could exert little mechanical effect on a gas, the molecules of which would pass freely through the jet in any direction.

If, however, a jet can be produced in which the molecules are moving not only in parallel directions, but also with nearly equal velocities, then collisions should disappear between the vapor molecules, even if the density of the vapor is far above the limit for ordinary molecular flow. Moreover, if collisions do occur, the resultant velocities must also be nearly equal and parallel, since[1] only the direction of the relative velocity, and not the velocity of the common center of gravity of the two molecules, is altered by the collision. A gas molecule moving with the jet could enter it readily, but would be effectively prevented from returning

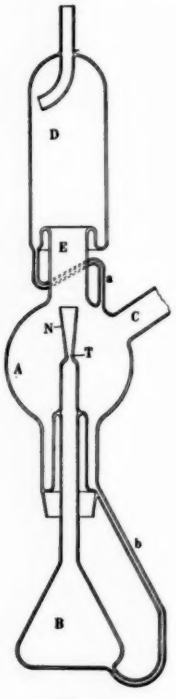

Fig. 1.

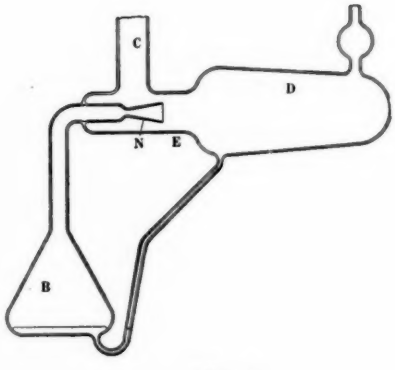

Fig. 2.

against the jet by the fact that it then meets a relatively enormous number of molecules, with some of which it must collide.

The line of thought indicated above led the author to try pumps of the form illustrated in Figs. 1 and 2. In Pump No. 6 (Fig. 1), the vapor generated in the boiler *B* at a pressure of 10 mm. of mercury or

[1] Maxwell, Scientific Papers, Vol. I, p. 377 et seq.

more, escapes through the narrow throat *T*, which, it will be noted, is at a considerable distance ahead of the point of entrainment. The vapor expands in the diverging nozzle *N*, and the issuing jet passes through the tube *E*, which it fills, and condenses in *D*, mostly, it is found, at the upper end. A slight amount of vapor escapes into the chamber *A*, and condenses there. The condensed vapor drains back through the tubes *a* and *b*, to the boiler. The gas to be pumped enters through *C*. Pump No. 5, Fig 2, is similar except as to arrangement, and the omission of the enlarged chamber *A* of Fig. 1, where its function is partly to condense the vapor arising from the mercury draining back from *D*.

The dimensions of the nozzle and passage *E* were about the same in the two pumps, viz.: Throat, 0.24 cm., mouth, 1.3 cm. diameter, ratio of areas, 30. Diameter of *E*, 2.5 cm., length, in No. 6, 5 cm., in No. 5 (measured from the end of *N*), 2.5 cm.

This form of nozzle is a result of the application of the principles of nozzle design used in steam engineering practice. As is well known, at the point of minimum area the pressure is never less than about half the initial pressure, the minimum pressure and maximum velocity occur in the diverging passage beyond the constriction. The reason for this difference from what takes place with a liquid lies in the expansive nature of the vapor.

It is found that a jet produced in this manner disperses only slightly, and will, if of a proper density, entrain the gas to be pumped even if the pressure of the gas is not over a thousandth of the computed internal pressure of the jet. No diffusion slit or condensing surface is necessary at the point of entrainment, in fact, the tube *E* surrounding the jet may be artificially heated to a point where no mercury can be seen condensing on it, without sensibly impairing the action. To all appearances the jet itself reëntrains and expels most of the vapor which is diffusely returned after striking the wall. The pumps are entirely air-cooled.

The theory of the formation of the jet appears to be that on account of the high initial pressure and the cooling due to the great ratio of expansion, the *relative* velocities of the molecules are much reduced, while they all acquire a very great common velocity in the direction of the jet. The absolute velocities are therefore nearly equal and parallel, as desired.

Certain properties of the jet in these pumps have been computed approximately, on the assumption that the vapor remains saturated, and neglecting friction, with the following results: Initial pressure, 18 mm., final pressure, 0.1 mm. Temperatures, 200 and 81° C., respectively. Velocity of jet, 42,000 cm. per sec. Relative molecular velocity, r.m.s. value, 21,000 cm. per sec. Mean free path, relative to jet, 0.08 cm.

If the free jet is 1 cm. long, each molecule is in it only 1/42,000 sec., in which time a molecule having the mean velocity will travel 0.5 cm. relative to the jet, and hence make only 6 collisions. Probably, due to the suddenness of the expansion and the absence of nuclei, the vapor enters the supersaturated condition, with a resultant lower temperature and lower relative molecular velocity, than that stated.

The fact that frictional effects do not destroy the jet suggests the explanation that the parallel motion reduces the number of collisions against the walls, both in the low pressure part of the nozzle, and in the compression passage *E*.

If the density of the jet exceeds a well-defined limit, the pump practically stops working, and the results approach those described by Langmuir for an aspirator with a dispersing jet. The author believes that this limit is established by the density of the dispersing fringe, which is probably proportional to the density of the jet, and occurs at the point where the mean free path of gas molecules entering the fringe becomes less than the total depth of the fringe.

TESTS.

In testing these pumps, the limitations of the apparatus available were such as to preclude obtaining extreme vacua. Pressures were measured on the intake side by a 500 c.c. McLeod gauge sealed to the pump through about 60 cm. of 1 cm. glass tubing, and on the discharge side by a 65 c.c. McLeod gauge, connected with glass tubing and rubber joints. The glass was not treated in any way, and the rate of fall of pressure, and the ultimate vacuum, were determined somewhat by the evolution from the glass and the friction in the tubing. The results were about the same with and without a drying agent (P_2O_5) in the vacuum space, the McLeod guage readings did not show symptoms of water vapor, indicating that the pump was effective in removing the latter.

The speed of the pump (cubic centimeters of gas per second at intake pressure) was determined by allowing air to leak in through a calibrated orifice located in the intake tube at a distance of 10 cm. from the pump, and was computed by the relation

$$S = \frac{760}{p} \times \frac{q}{1000},$$

where p = pressure in vacuum space, millimeters of mercury,

q = rate of leakage, cu. mm. per sec., measured at 760 mm. pressure.

The speed is therefore that of the pump in series with 10 cm. of tubing, 19 mm. in diameter.

Results.

Pump No.	Observation No.	Boiler Pressure, Mm.	Leakage, Cu. Mm. per Sec. q.	Pressure, Mm.		Speed C.c., S.
				Discharge.	Intake p.	
4	1	38	0	0.014	0.00002	——
	2	114	0	0.017	0.00004	——
	3	117	0	0.090	0.00002	——
	4	102	0.84	0.035	0.0061	105
	5	108	1.76	0.055	0.00105	1270
5	6	33	3.14	0.027	0.15	16
	7	27	2.0	0.024	0.11	16.5
	8	22	1.5	0.020	0.035	31.5
	9	21	1.6	0.019	0.013	93
	10	16	1.8	0.025	0.0025	550
	11	12	2.2	0.022	0.0026	640
	12	7	1.6	0.030	0.0021	580
	13	5	1.8	0.019	0.0029	470
	14	3	1.25	0.013	0.0058	164
	15	2	1.76	0.019	0.0086	155
	16	1	1.78	0.019	0.017	80
	17	16	0	0.057	0.00005	——
6	18	25	0	0.080	0.0001	——

Observations 6 to 16 inclusive are plotted in Fig. 3.

Pump No. 4 resembled No. 6 except that the nozzle had half the linear

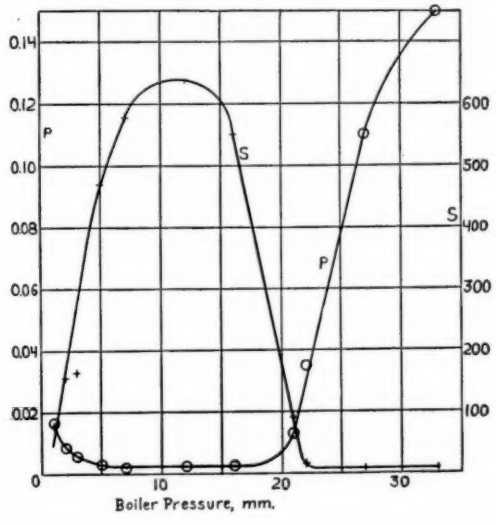

Fig. 3.

dimensions, and the chamber A was narrow, becoming heated by conduction and radiation from the vapor tube, and forcing the retrograde vapor to pass up into C before condensing. This was the condition in reading No. 4. A slight amount of cooling on A had the effect of greatly increasing the speed (reading 5). Cooling E as well as A gave little further increase in speed (perhaps 20 per cent.). Decreasing the radiation from E by wrapping it in cotton wool caused the mercury previously condensed on the wall to slowly reëvaporate, but while this was occurring the speed was not sensibly reduced. In readings 1 to 3 the pump was not cooled.

In all the readings given for No. 5, the passage E was electrically heated and no visible condensation took place in it. Even without this heating, relatively little mercury condenses here, but it was desired to prove that condensation was not a factor in the entrainment. These readings show clearly the necessity of the jet density lying within well-defined but not necessarily narrow limits. The ratio of expansion being fixed by the nozzle, the density of the jet may be considered as proportional to the boiler pressure. Simultaneously with the reduction of the speed by high boiler pressure, retrograde vapor could be seen condensing rapidly in C. The effect of too low density is also shown.

Only meager tests were made on No. 6, which was connected to the apparatus through narrow rubber tubing, preventing a favorable determination of the speed. This pump seemed to produce good results with a slightly higher boiler pressure than No. 5, indicating the usefulness of chamber A in rarefying and condensing the retrograde vapor, permitting the gas to be entrained despite the higher jet density.

The following comparison of the speed of these pumps with the values stated by Langmuir for the condensation pump is of interest.

Style.	Diameter, Cm.	Speed, C.c. per Sec.	Ratio Speed/Diam.^{2}.
Condensation.....	2.0	200	50
Parallel jet No. 5.....	2.5	500	80
Parallel jet No. 4.....	2.5	1200	192
Condensation.....	7.0	3000	61

It is probable that the jets in Nos. 4 and 5 are not the best that can be produced by this method, and that with slightly different proportions, greater speeds can be obtained with tubing of the same size. The speed of the intake passages of No. 5, computed by Knudsen's formula, is about 5,000 c.c. per sec., the difference is to be attributed to the resistance of the jet to the entrainment of the gas.

The work reported herein was done partly at the local laboratory of the Victor Electric Corporation, of Chicago, and partly at the University of Pennsylvania. The author wishes to express his thanks to Mr. H. Clyde Snook, and to Dr. Harold Pender, for suggestions, encouragement, and facilities.

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A DETERMINATION OF THE EFFICIENCY OF PRODUCTION OF X-RAYS.

BY PAUL T. WEEKS.

THE purpose of this investigation was to measure the energy of the X-rays emitted by a Coolidge tube by means of their heating effect; to determine the efficiency of production of X-rays, *i. e.*, the ratio between the energy of the X-rays and the energy supplied to the X-ray tube; and to determine the variation of this efficiency with the potential across the tube.

A variety of methods have been used for the measurement of X-ray energy.

The first measurement was made by Dorn[1] in 1897 by means of a differential air thermometer. A bolometer method was used by Schöps[2] in 1899, by Rutherford and McClung[3] in 1900, by Wien[4] in 1905, by Angerer[5] and Carter[6] in 1906. Bumstead[7] in 1906 measured the energy by means of a radiometer and Adams[8] in 1907 used a radiomicrometer. A thermopile was employed by Wien[4] and by Hoepner[9] in 1915. In several cases the energy supplied to the tube was not determined so that no conclusions could be drawn as to the efficiency of production of the X-rays. Wien,[4] Angerer,[5] and Carter,[6] however, measured the energy carried by the cathode rays and determined the value of the efficiency. Carter also determined the variation of the efficiency over a considerable range of voltage.

The ionization produced by X-rays has also been used as a means of determining the efficiency of production of the X-rays. Rutherford and McClung[3] early found a value for the energy required to produce an ion in air by X-rays. In 1913 Beatty[10] determined the number of ions produced by the total absorption of X-rays. From the work of

[1] Wied. Ann., 63: 160.
[2] Dissertation, Halle.
[3] Proc. Roy. Soc., 67: 245.
[4] Ann. d. Phys., 18: 991.
[5] Ann. d. Phys., 21: 87.
[6] Ann. d. Phys., 21: 955.
[7] Phil. Mag., 11: 292.
[8] Proc. Am. Acad., 42: 671.
[9] Ann. d. Phys., 46: 577.
[10] Proc. Roy. Soc., 89: 314.

others he computed the total number of ions which would have been produced directly by the cathode rays which excited the X-rays. The ratio of these two quantities he took as the efficiency of transformation of energy from cathode rays to X-rays. He gives the following relation as the result of his work: $\frac{\text{X-ray energy}}{\text{cathode ray energy}} = 5.1 \times 10^{-5} A\beta^2$, where A is the atomic weight of the metal of the anode and β is the ratio of the velocity of the cathode rays to the velocity of light. In 1912 Eve and Day[1] determined the total number of ions produced in air by X-rays and found a value for the efficiency of production of X-rays from the energy supplied to the tube and the energy required to produce an ion, as determined from other experiments. Recently, 1915, Rutherford and Barnes[2] have made a determination of the energy output of a Coolidge tube from the total number of ions produced and the energy required to produce an ion by alpha rays. The energy supplied to the tube was measured and from this the efficiency computed.

Below is given a summary of the results of previous work. The values of the efficiency given are computed for the total energy which would appear on the outside of the tube on the supposition that the energy is emitted equally in all directions throughout a whole sphere.

Observer.	Method.	Potential.	Efficiency.
Wien	Bolometer	58.7 K.V.	.00143
Wien	Thermopile	58.7	.00183
Angerer	Bolometer	Low	.0004
Carter	Bolometer	59	.00062
Hoepner	Thermopile	65	.00029
Eve & Day	Ionization	(11 cm. gap)	.0001
Rutherford and Barnes	Ionization	48	.00059
Beatty	Ionization	48	.0019
(Abs. only by thin Al.)		59	.0023

In view of the differences in the values obtained by the various observers by means of the heating effect it seemed to be desirable to make a new determination under the more favorable conditions of better control of current and potential and larger power input made possible by the Coolidge tube.

Description of Apparatus.

A bolometer method was used, one of two similar resistances being exposed to the X-rays and the relative change in its resistance caused

[1] Phil. Mag., 23: 683.
[2] Phil. Mag., 30: 361.

by the heating effect detected by means of a Wheatstone's bridge and a galvanometer. The resistances were made of .056 mm. lead foil cut in grid form and folded back and forth on itself so as to form a continuous screen of about 1 mm. thickness which would absorb almost completely the incident radiation. Thin paper was used for the insulation between layers. The resistance of the grid which was exposed to the X-rays was 4.35 ohms and of the other 3.87 ohms. To protect the resistances from fluctuations in room temperature they were enclosed in a Dewar cylinder as shown in Fig. 1. The resistance to be exposed, called A, was placed in front of the comparison resistance, B. Between them was placed a 2 mm. lead screen and in front of A a similar screen with an opening 6.5 by 6.45 cm. This was 29.4 cm. from the target, so that it subtended /251.5 of the whole sphere. The end of the Dewar was closed with a cardboard .85 mm. thick. The Dewar was enclosed in a wood box and the end packed with wool to reduce the conduction of heat.

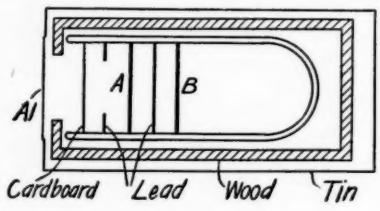

Fig. 1.

A D'Arsonval galvanometer was used, of the Leeds and Northrup high voltage sensitivity type. This was connected with a shunt so as to be very nearly critically damped. With a measuring current of .07 ampere a change of one thousandth part in the bridge ratio gave a deflection of 250 cm. at a scale distance of 4.8 meters. The entire bridge circuit was enclosed in a grounded metal cage to prevent inductive disturbances. The part of the cage in the path of the beam of X-rays was formed by a sheet of aluminum .09 mm. thick, which served also to cut off all direct heat radiation from the tube.

High potential uni-directional current was secured by means of a closed core transformer and mechanical rectifier. The tube current was measured by means of a D.-C. milliammeter. The filament of the X-ray tube was heated by means of a lead storage battery. For measuring the potential across the tube a sphere gap was first used. This was found to be unsatisfactory for measurements during the course of a run but served for calibrating. The sphere gap consisted of two brass spheres, each 6.5 cm. in diameter, placed horizontally. Each of these was connected to the line through a resistance of distilled water, the total resistance in series with the gap being of the order of 10 megohms. A tendency for the potential to rise to an abnormally high value before spark-over would occur was almost entirely eliminated by placing a tube containing some radium bromide close to the gap. For indicating

the potential during the course of a run a balance form of electrostatic voltmeter was constructed. The movable part of this, a 4 cm. sphere, was suspended from a spiral spring and was immersed in oil above a flat metal plate. This voltmeter was easily read and was found to follow small changes in the potential with practically no lag.

METHOD OF OBSERVATION.

Due to the inequality of the two resistances the measuring current produced a change in the resistance ratio. In addition there was unequal heating in the two from the stray heat conducted in from the outside. Consequently there was a continual drift of the spot of light. However this was not erratic and the rate was determined before each exposure by taking four or five readings at one-minute intervals. The rate of drift could be kept within the desired limits by varying the room temperature slightly. The time between exposures was ordinarily eight to ten minutes as it was necessary to wait for the target to cool as well as to determine the rate of drift.

Exposures were made for 30 seconds, the current and potential being held nearly constant during this time. In Fig. 2 is given a curve showing the galvanometer deflections during a typical exposure, the circles indicating the readings taken. Some corrections were necessary in determining from these readings the actual rate of heating due to the absorbed X-rays. By taking account of the rate of drift it was possible to determine the deflection due to the absorbed X-rays only. Then from the observed rate of cooling during the first 15 seconds after the exposure it was possible to correct for the cooling which took place during the exposure. Thus in the case shown in Fig. 2 the deflection due to the X-rays only was taken to be 6.90 cm. at the end of the exposure and 5.96 cm. 15 seconds later. These values give 15.95 cm. per minute for the rate of deflection due to the X-rays alone. From this rate of deflection and the heat sensibility of the bolometer, determined later, the amount of energy absorbed could be computed in joules per ampere-second of tube current. This multiplied by 251.5 gives the energy for the whole sphere.

A set of 5 to 10 exposures was made at one current and potential and then the tube adjustment changed or a different absorbing screen inserted in the path of the rays and a similar set obtained. For each potential several such sets were made on different days and with different values of tube current. Readings were taken at eleven different potentials and at four of these readings were taken with four different thicknesses of aluminum in the path of the rays for the purpose of determining the

absorption curves. The results for each potential were derived from at least 20 and in some cases 40 separate exposures. For the absorption curves only from 10 to 20 exposures were made with each screen at each potential.

CALIBRATION OF THE BOLOMETER.

The heat sensibility of the bolometer was determined by sending through the resistance *A* a known current for 30-second intervals and observing the resulting galvanometer deflections. While the heating current was flowing the measuring circuit was kept open. Readings were taken similar to those taken in the determination of the heating due to the X-rays and similar corrections were made. The heat produced in resistance *A* was computed from its resistance and the current flowing in it. Since *A* was in parallel with part of the bridge resistance the observed value of the current had to be corrected for the small current which flowed through the bridge. The mean sensibility obtained was 50 cm. per joule per .07 ampere measuring current.

MEASUREMENT OF THE ENERGY SUPPLIED TO THE TUBE.

If the tube had been operated by steady direct current it would have been sufficient to take the product of the tube current and the potential across the tube as the power supplied to the tube. However in the case of the rectified alternating current the current and voltage were both pulsating and the wave form of neither was known. Furthermore the voltmeter deflections were determined by the root mean square value of the potential and the milliammeter deflections by the mean value of the current. Therefore it was thought advisable to make a direct determination of the power by means of the heating effect.

The method employed was to immerse the tube in an oil bath and measure the energy supplied by means of the rise in temperature of the oil. The tank was made of tin and was enclosed in a wood box. It was just large enough to contain the tube and allow of sufficient insulation. Kerosene oil was used for the bath. The tube was covered over with a black insulating cloth which was also immersed in the oil. A small propeller driven by a motor served to keep the oil well stirred. The rise in temperature was indicated by means of two copper-advance thermocouples, two junctions being placed in different parts of the tank and two in a container of oil outside. The thermojunctions were connected in series with the galvanometer used in the previous measurements and with 950 ohms resistance and gave about 17 cm. deflection per 1° C.

Continuous runs were made, the potential and current being kept as nearly constant as possible and galvanometer deflections being noted

every minute. The duration of each run was from 15 to 20 minutes and the rate of heating between 4 and 5 cm. per minute. The rate of cooling was found before and after each run and the mean added as a correction to the observed rate of heating. Several runs were made and gave concordant results. The tube potential was kept at 31.6 K.V. and the current at 4.80 m.-a. It was intended to make runs at other potentials, but at this point the tube developed a leak and could not be used further.

Observations were next made on the heating produced by sending current through a heating coil placed in the bottom of the tank. Conditions were kept as nearly as possible the same as before, the stirring device being kept in operation and the tube filament lighted. The current through the coil and the potential difference across its terminals were measured at intervals throughout the run. Runs were made with the power adjusted to give heating at rates somewhat above and somewhat below that produced by the operation of the tube. These gave 188 watts as the power corresponding to a tube potential of 31.6 K.V. and a tube current of 4.80 m.-a.

Calibration of the Voltmeter.

The voltmeter was calibrated by means of the spark gap and an electrostatic balance. This latter could be used only for the lower voltages on account of spark-over. It was found that a given voltmeter reading corresponded to a 20 per cent. higher R.M.S. potential, as determined by the balance, with rectified current than with alternating current. The difference was somewhat larger according to the spark gap readings but approached the same value at higher potentials. The oscillations introduced by the rectifier were probably responsible for the lower spark-over potentials with the rectified current. The differences in the voltmeter readings with alternating and rectified current were undoubtedly due to a leakage of charge over the surface of the glass jar containing the oil in which the attracted sphere was immersed. This would change the distribution of the field and so change the vertical force on the attracted sphere. A comparison of alternating potentials as determined by the electrostatic balance and by the spark gap indicated that the transformer used gave a wave form having a peak value 7 per cent. higher than a sine wave of the same R.M.S. value. The spark gap potentials used were those given by Peek[13] for 6.25 cm. spheres. The final calibration of the voltmeter was then determined from the

[13] "Dielectric Phenomena," by F. W. Peek; same in A. I. E. E. Standardization Rules, 1915.

alternating current spark-over voltages with the corrections indicated above.

COMPUTATION OF EFFICIENCIES.

In the experiment to determine the power supplied to the tube it was found that with a potential of 31.6 K.V. and 4.80 m.-a. current the power supplied was 188 watts. The product of kilovolts and milliamperes is 152. This gives a correction factor of 1.24. Inasmuch as the milliammeter read mean values of the current a rectified sine wave voltage and current would have given a factor larger than unity, but the large value found under the conditions of the experiment is surprising. It would have been desirable to determine this factor for other voltages. The efficiency of production of the X-rays was taken to be the ratio of the total number of joules of X-ray energy given out per ampere-second to the number of watts supplied per ampere. The values found for the efficiency are given in the fourth column of Table I.

TABLE I.

R. M. S. K. V.	Input $\frac{\text{Watts}}{\text{Amp.}}$	Obs. X-Ray Energy $\frac{\text{Joules}}{\text{Amp.-sec.}}$	Efficiency without Correction.	Absorption Factor.	Total Energy $\frac{\text{Joules}}{\text{Amp.-Sec.}}$	Total Efficiency.
28.3	35.1×10^3	17.1	0.49×10^{-3}	1.20	20.5	0.58×10^{-3}
31.6	39.2	23.4	0.60	1.17	27.4	0.70
34.5	42.8	30.7	0.72	1.15	35.3	0.82
37.1	46.0	38.3	0.83	1.13	43.2	0.94
39.5	48.9	46.3	0.95	1.11	51.3	1.05
41.6	51.5	52.3	1.02	1.10	57.5	1.15
43.5	53.9	59.3	1.10	1.09	64.6	1.20
45.2	56.1	66.9	1.20	1.08	72.3	1.29
48.2	59.8	84.3	1.41	1.07	90.2	1.51
50.8	63.0	93.6	1.49	1.07	100.2	1.59
53.9	66.8	118.0	1.77	1.06	125.1	1.87

CORRECTION FOR ABSORPTION.

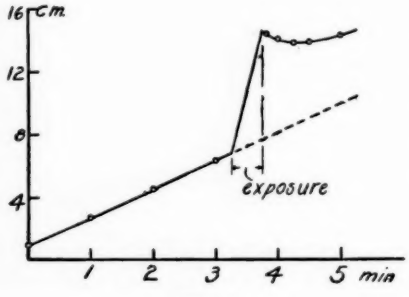

Fig. 2.

To determine the correction for the absorption in the screens which were in the path of the X-rays absorption curves were obtained for four different potentials. The results are shown in Fig. 3, Curves *A*, *B*, *C* and *D* corresponding to R.M.S. potentials of 50.8, 45.2, 39.5, and 31.6 K.V. respectively. These are plotted as percentage transmission

against thickness of aluminum in millimeters. In the path of the rays was an aluminum screen .09 mm. thick and a cardboard screen .85 mm. thick. This latter was estimated to be equivalent to .08 mm. of aluminum. In Fig. 3 a line is drawn at the left of the axis at a distance corresponding

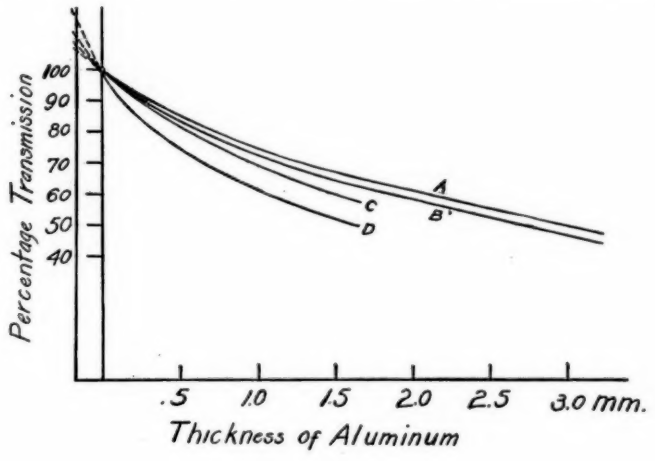

Fig. 3.

to .17 mm. and the absorption curves are continued to intersect this. The intercepts on this line give the correction factors for determining the total efficiency. The correction factors for intermediate potentials were found by interpolation. These values are given in the fifth column of Table I. In the seventh column are given the values of the total efficiency for the total energy outside of the tube. It is evident that no accurate estimate can be made of the energy absorbed in the walls of the tube.

Discussion of Results.

In Curve *A* of Fig. 4 is shown the variation of the efficiency, uncorrected for absorption, with the potential. In Curve *B* is shown the variation of the corrected efficiency with the potential. The shape of these curves is similar to that given by Carter.[6] It seems very possible that if correction for absorption in the tube could be made the efficiency might be found proportional to the potential as required by Beatty's formula (see p. 2). In Fig. 5 the efficiency is plotted against kilovolts squared, Curve *A* giving uncorrected values and Curve *B* the values corrected for absorption. From these it would seem that the X-ray energy emitted through the tube is nearly proportional to the cube of the potential. The fact that the photographic effect is proportional to the square of the potential, as found in practice, may be explained on the

ground that the harder rays are absorbed to a less extent in the photographic emulsion and are also less effective because their wave-lengths are much less than those of the characteristic radiations of bromine and silver.

A comparison of the results given here with those obtained by other

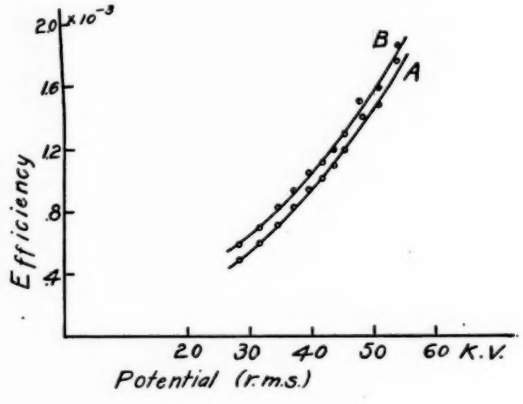

Fig. 4.

observers using the heating effect shows that the values of the efficiency are higher in general than those previously given. According to Rutherford and Barnes[12] Beatty's values should be divided by a factor of 2 or 3 for comparison with the other values given because in his experiment

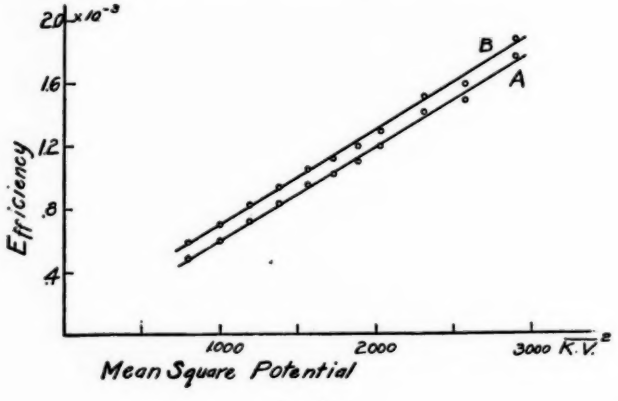

Fig. 5.

the X-rays did not pass through the glass wall of the tube but only through a thin aluminum window. Both Carter and Wien used an induction coil and measured the potential by means of a spark gap which would give very nearly peak values. It would seem that their values for

59 K.V. should be compared with a value given here for a potential between 40 and 50 K.V. On this assumption the results given here are somewhat below the corresponding results given by Wien and considerably above those given by Carter.

The values of the efficiency found are quite different from those found by ionization methods. The results given by Rutherford and Barnes are based on a value for the energy required to produce an ion which was determined from measurements with alpha rays. This was taken to be the same as the energy required to produce an ion by means of X-rays. A similar assumption is involved in Beatty's results, namely, that the same amount of energy is required to produce an ion by means of cathode rays as by X-rays. The work of Barkla and Philpot,[1] of Wilson[2] and of others[3] would indicate that ionization by X-rays takes place through the intermediate production of high-speed electrons. Hence the assumption made by Beatty seems justified if all the energy of the X-rays is given to these electrons. This has not been proven definitely. The work of Kleeman[4] indicates approximate proportionality between the ionization produced in different gases by alpha, beta and gamma rays. The work of Rutherford and Robinson[5] showed that in the case of alpha and gamma rays from radium C the heating and ionization were nearly proportional, although there were large errors involved. If this proportionality is accepted as established it would seem to justify the assumption made by Rutherford and Barnes in their determination of the efficiency of production of X-rays.

However if we compare the values for the energy required to produce an ion as found in this way and the values found by other means there are seen to be large discrepancies. A recent determination by Bishop[6] gives 1.67×10^{-10} ergs per ion, or one third of that given by Rutherford and Barnes, 5.1×10^{-11} ergs (33 volts). Using this value for the energy to produce an ion Rutherford's and Barnes's value for the efficiency of production of X-rays becomes $.2 \times 10^{-3}$ for 48 K.k. The value given by Eve and Day is based on an energy of 2×10^{-11} ergs per ion and is thus seen to be in fair accord with this as they used a somewhat lower potential. The value for ionizing energy obtained by Rutherford and McClung,[3] when corrected for the large value for "e" used by them, is 1.4×10^{-11} ergs per ion. The work of Rutherford and Barnes shows

[1] Phil. Mag., 25: 832.
[2] Proc. Roy. Soc., 87: 277.
[3] Bragg, "Studies in Radioactivity," Chapter 12. See also (14).
[4] Phil. Mag., 14: 618.
[5] Phil. Mag., 25: 312.
[6] PHYS. REV., 33: 325.

that at 48 K.V. there would be produced by a Coolidge tube 12×10^{13} ions per second per watt input. Using the value of efficiency found in the present investigation this would correspond to an X-ray energy of 1.5×10^{4} ergs per second or 1.25×10^{-10} ergs per ion, a value nearly the same as that found by Rutherford and McClung by a similar method.

From these four investigations it would appear that the energy of the ions produced by X-rays is only a fraction of that emitted from the tube in the form of X-rays. To a less extent the same thing is true of alpha rays which appear to be more efficient than X-rays in producing ionization. These conclusions seem to contradict the evidence given by experiments with radioactive materials. To decide the point the heating effect and the total ionization should be determined simultaneously or under the same conditions.

SUMMARY.

The energy given out in the form of X-rays by a Coolidge tube has been determined by means of a bolometer. The values found lie between 20 and 125 joules per ampere-second for potentials between 28 and 54 K.V.

The energy supplied to the X-ray tube has been measured by its heating effect.

The ratio between the X-ray energy and the energy supplied to the tube, or the efficiency of production of the X-rays, has been found for these potentials. This ratio varies between 0.58 and 1.87×10^{-3}.

The X-ray energy is found to be nearly proportional to the cube of the potential across the tube.

A comparison of these results with those obtained by others on the total ionization produced by X-rays indicates that only a fraction of the energy of the X-rays is transformed into the energy of the ions produced on total absorption in air.

I wish to express my indebtedness to Professor J. S. Shearer and to other members of this department for suggestions and help given me and for the apparatus put at my disposal.

CORNELL UNIVERSITY,
June, 1917.

THE WAVE-LENGTH OF LIGHT FROM THE SPARK WHICH EXCITES FLUORESCENCE IN NITROGEN.

By Charles F. Meyer.

IT was shown by Professor Wood[1] in 1910, that radiations from the aluminium or copper spark are capable of exciting ultra-violet fluorescence in air and other gases, notably in nitrogen. The spark was passed between a rod serving as lower terminal, and a plate with a small hole in it serving as upper terminal, the spark striking just at the edge of the hole (Fig. 1). All the radiations from the spark, including the visible and ordinary ultra-violet, pass up through the hole in the plate, and if any of the radiations cause fluorescence this can be photographed by placing a camera off to one side of the opening. The luminosity was first photographed with a camera fitted with a quartz lens, and then with a quartz spectrograph which had had its slit removed, the fluorescent jet itself serving as slit.

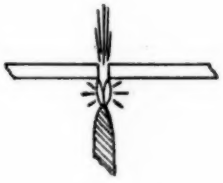

Fig. 1.

It was shown that the fluorescence in air consisted of the water bands 3064 and 2811, principally the former. When an atmosphere of nitrogen was used above the plate the water band 3064 appeared, and also the three nitrogen bands 3369, 3556 and 3778.

Inquiring now into the origin of the luminosity which exists above the opening, it is evident that the luminosity cannot arise from the simple scattering of light from the spark by particles of dust, or by the air molecules, as the spectrum of the luminosity is quite distinct from that of the spark, and a quartz plate several millimeters thick, placed over the hole, causes the light to disappear entirely.

That the fluorescence is excited by light in the Schumann or ultra-Schumann region was the first hypothesis proposed by Professor Wood, and in some work by Wood & Hemsalech[2] it was shown that the radiations were transmitted, but only to a slight degree, by a thin piece of clear fluorite. This fact indicated that the radiations exciting the fluorescence lay beyond the Schumann region, for the limit of the

[1] Phil. Mag. (6), Vol. 20, p. 707.

[2] Phil. Mag. (6), Vol. 27, p. 899, 1914.

Schumann region is set by the transmission of fluorite in sufficient thicknesses to form prisms and lenses.

Wood & Hemsalech also showed that the radiations exciting the nitrogen bands were transmitted to a slight degree through quartz, and in some experiments which Professor Wood and I performed,[1] we refracted the radiations through the extreme edge of an especially ground quartz prism, the path in the prism being probably less than a tenth of a millimeter. The index of refraction for the radiations came out $1.75 \pm .08$, that is, with a probable value greater than that of quartz at the more refrangible end of the ordinary ultra-violet. This value of the index of refraction made it seem as though the radiations were still on the long wave-length side of the quartz absorption band, and possibly not far beyond the limit of the Schumann region, if indeed they were beyond it at all. Unless it should be that they were on the long wave-length side of an entirely hypothetical second absorption band of quartz well beyond the Schumann region.

At this time we also succeeded in reflecting the radiations from silicon and speculum. The reflection experiment put me in mind of a method by which the wave-length of all or a part of the radiations might be approximately determined, in case they had a wave-length of seven or eight hundred angstroms or more.

The method is as follows: A very fine slot (.2 x 2 x 4 mm) is cut in a copper rivet, copper now being used for the spark terminals throughout. Beneath this is fastened a small fragment of a grating with the lines horizontal and parallel to the edges of the slot. The rivet serves as one spark terminal, a copper rod or wire as the other. Fig. 2 represents this arrangement in vertical section, *R* is the rivet with the slot in it. The rivet is driven through the thin copper plate *C*. *S* is the rod serving as the other spark terminal. *G* is the small fragment of a grating, the lines being perpendicular to the plane of the drawing. The plate *C* is bent into a right angle and fastened to an arm *A* which rotates on a horizontal axis. This rotation allows the plate, the rivet, and the grating, which are all fastened rigidly together, to be raised for the purpose of cleaning the grating. Below the grating and the lower end of the plate *C* is a thin horizontal plate with a rectangular hole in it 3 mm. by 4 mm. This second plate forms the top of a metal box into which nitrogen is introduced. The box also serves to keep out stray light and thus yield a dark background. The apparatus is represented in perspective in Fig. 3. The lettering of the parts is the same as in Fig. 2, only in addition attention is now called to the representation of the upper portion of the

[1] Phil. Mag. (6), Vol. 30, 1915.

box B, with the quartz window W, and some ten centimeters in front of the window the lens L and the prism Pr, and finally, off at a small angle, the photographic plate P. The path of the central ray through the optical system is indicated in the diagram. To avoid confusion in the diagram, a metal tube of about 2 cm. diameter, through which nitrogen

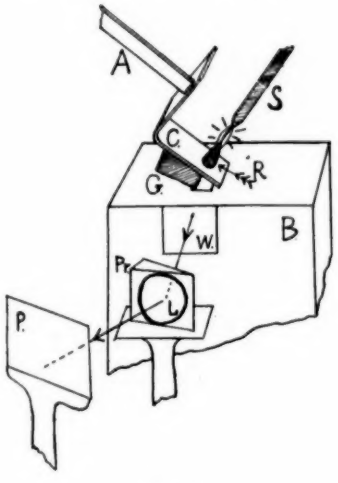

Fig. 2.

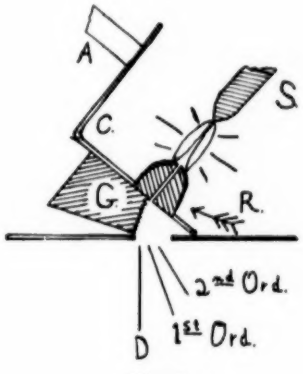

Fig. 3.

is introduced into the rear of the box B, has been omitted from the drawing. This tube also helps give an absolutely dark background, which is essential. None of the drawings are to scale, some dimensions being exaggerated for the sake of clearness.

Referring again to Fig. 2, it is seen that the beam of light, which comes through the slot in the rivet, strikes the grating at a large angle of incidence (73 deg.). The directly reflected beam comes off in the direction D in the figure. The first and second order diffracted beams come off in the directions indicated. The exciting light causes fluorescence along these three paths, and this fluorescence is photographed by the optical system represented in Fig. 3. The object of the 30 deg. prism Pr, is only to disperse the fluorescent light slightly and thus have a check on the nature of the spectrum, and to be certain that there is no scattered light. The prism is set for minimum deviation.

The dispersion caused by the prism would create confusion in the directly reflected and the diffracted beams if the fluorescent spectrum were a complicated one. But by using commercial nitrogen slightly moistened it is possible to limit the fluorescence to the water band 3064 alone. Moist nitrogen was used in the experiments.

The first experiment of this kind was made over a year ago, with a

grating of 15,000 lines to the inch. But the diffracting angle was not very great with this and it was felt that the experiment should be repeated. This has recently been done, using a grating of 30,000 lines to the inch. The results are much better, both on account of the more suitable grating and on account of improved technique. Measurements made upon two plates yield a result of 1300 Å., with a probable error of some 50 or 70 Å. This is for the wave-length of the light exciting the fluorescence of the water band 3064. The measures of course do not admit of much accuracy, as the beams of fluorescent light are not sharply bounded and not as intense as might be desired. The measures are made on the first order beam. An exposure of six or seven hours is necessary, the exposure being interrupted every half hour for cleaning the grating. The best plate shows also the second order diffracted beam quite unmistakably.

The experiment with the fluorescence in nitrogen was checked by placing a piece of cardboard in the chamber below the grating, the cardboard lying in the plane of the drawing (Fig. 2). The light scattered by the cardboard was photographed through the same optical system, but passing in addition through a film of silver on quartz which allowed only light of the wave-length of the silver transmission band to pass. The wave-length calculated in this manner for the transmission band of silver came out quite within the limit of experimental error.

As a result of the entire set of experiments it seems fairly certain that at any rate some of the radiations previously studied lie at the border of the Schumann region, and not beyond it. But it is difficult to account for the rather low transparency of good fluorite for the radiations, and the transparency of the air seems greater than would be expected. No actual measurements have been made of the transparency of the air. Professor Wood suggests that the fluorescence may be excited simultaneously by the radiations whose wave-length I have measured and by some of shorter wave-length which are not readily transmitted by fluorite or reflected by speculum metal. This may well be true.

It seems worth while, also, to consider the supposition that the radiations whose wave-length was measured are the only ones causing fluorescence. In this case it is necessary to suppose that the transparency of the fluorite is lessened, due to its proximity to the spark and consequent heating, and there remains to investigate the transparency of the air. It was hoped to do this, and to see whether there might possibly be an effect of the spark upon the transparency of the air in its immediate vicinity, but it has become necessary to lay the work aside for an indefinite period.

A rough estimate may be made from the reflection experiments of the coefficient of reflection of speculum metal for the region near 1300 Å. It seems to lie between 5 and 10 per cent. at 75 deg. incidence.

In conclusion, I wish to thank Professor Wood for making several helpful suggestions.

PHYSICAL LABORATORY,
UNIVERSITY OF MICHIGAN,
June, 1917.

A STUDY OF APPARENT SPECIFIC VOLUME IN SOLUTION.

BY LEROY D. WELD AND JOHN C. STEINBERG.

IV. RESULTS WITH COPPER SULPHATE.

IN a former paper,[1] of which this is a continuation, one of the authors has outlined the problem and explained the experimental methods used, and presented the results obtained from experiments upon solutions of potassium chlorate. For convenience, the matter may be summarized as follows:

The *apparent specific volume* of the dissolved solute, designated by Δ, is defined as *the volume of the solution containing one gram of the solute, minus the natural volume of the pure water entering into it at the same temperature.* The variations of Δ with temperature at constant concentration, and with concentration at constant temperature, in the case of potassium chlorate, were set forth in the former paper, the experimental arrangements being such as to follow with the most minute accuracy changes in the density of the solution. The results gave strong indication of a *minimum volume in solution*, and the minimum was actually reached in one super-saturated solution. This is strongly suggestive of the behavior of water, pure or in mixture with dissolved substances, in the neighborhood of freezing.

This research has been taken up by Mr. Steinberg and applied to copper sulphate, with such modifications in procedure as have been found necessary owing to the radically different properties of the substance under examination.

Copper sulphate is about three times as soluble as potassium chlorate, and crystallizes with five molecules of water, whereas potassium chlorate is anhydrous. The solutions of copper sulphate can be much further super-saturated, that is, cooled much further below the saturation temperature without crystallizing out, and then the crystals form very slowly, growing in large masses at the bottom of the vessel, instead of suddenly forming in the solution and settling down like snowflakes, as do those of potassium chlorate. The specific volume in solution, Δ, for copper sulphate turns out to be very much less than for potassium chlorate, and it decreases with increasing concentration in saturated solution.

[1] L. D. Weld, PHYS. REV., N. S., Vol. 7, p. 421.

In preparing the stock solutions, small batches were at first made up just before using, at approximately the concentration desired, and specimens therefrom carefully analyzed to determine the exact strength. Later an electrically controlled thermostat was constructed, in which

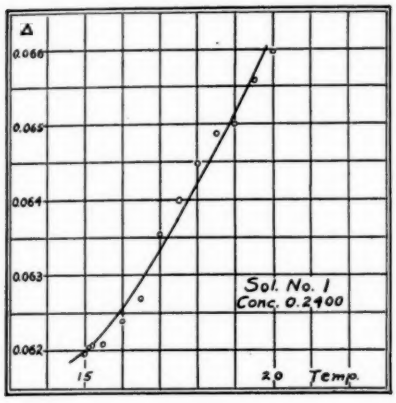

Fig. 7.

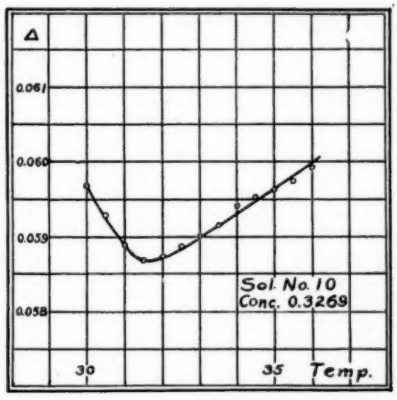

Fig. 8.

large flasks of stock solution could be kept at any desired temperature for days, tightly stoppered and without crystallizing or evaporating.

The analyses were made electrolytically, the solution from which the copper was deposited being stirred during electrolysis by the mechanical

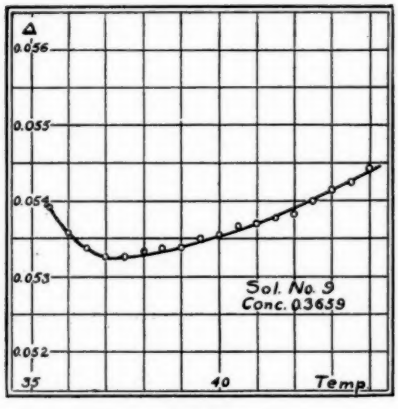

Fig. 9.

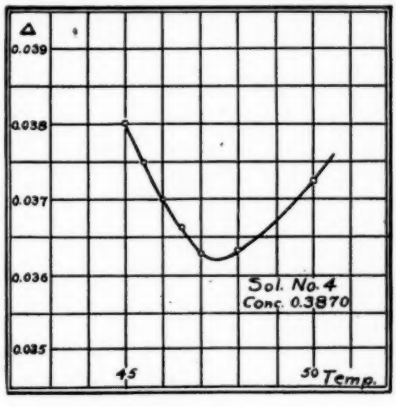

Fig. 10.

action of a strong magnetic field passing through the current-bearing liquid.

Series of experiments made upon these solutions at several different concentrations gave results which exhibit the minimum specific volume in solution in the most striking manner, being far more pronounced than

any obtained previously with potassium chlorate. Four of these series are shown graphically on the accompanying diagrams, which correspond to the curves in Fig. 4 of the former section. Only the first of these, that at concentration 0.24 (Fig. 7), was stopped too soon to exhibit the actual minimum, whereas in the former research, only one was obtained that did clearly exhibit it.

It is hardly necessary to enlarge upon the support which these later results give to the theory previously suggested. The existence of the minimum specific volume in solution can hardly be questioned. And it further appears in this case, as in that of potassium chlorate, that the temperature of this minimum is lower, the more foreign substance (water) there is in mixture with the substance under examination (copper sulphate). In fact, the phenomenon presents so many points of similarity to those of the minimum volume of pure and solvent water as to lead one to suspect very strongly that the phenomena are identical in nature, whether to be explained on the Roentgen complex molecule hypothesis or otherwise.[1]

COE COLLEGE,
CEDAR RAPIDS, IOWA,
June, 1917.

[1] See discussion at the bottom of p. 428 of the former paper, loc. cit.

THE ABSORPTION OF MERCURY VAPOR BY TIN-CADMIUM ALLOY.

BY L. A. WELO.

THE writer has been engaged during the past year in a spectroscopic study of the gases occluded in certain metals, and has had occasion to keep the vapors from the mercury pump out of the evacuated tubes by cooling the intervening connections in liquid air. An accident to the liquid-air plant threatened to delay the work, as no gold leaf was at hand to be used as a substitute, until it was suggested by Dr. L. T. Jones that a portion of the connecting tubing be packed with some of his supply of chips of a tin-cadmium alloy which is known to form an amalgam with great ease. The alloy, commonly known as dentist's amalgam, consists of two parts of tin to one of cadmium and was used in the form of chips cut from a bar of the alloy with a milling machine. They have a thickness of the order 0.05 mm., are 12 mm. in length and vary in width from 1 to 3 mm.

A special test of the material has since been made to establish upper and lower limits for the length of tubing to be packed. The apparatus is shown in the figure. Eight branches are blown on centimeter tubing

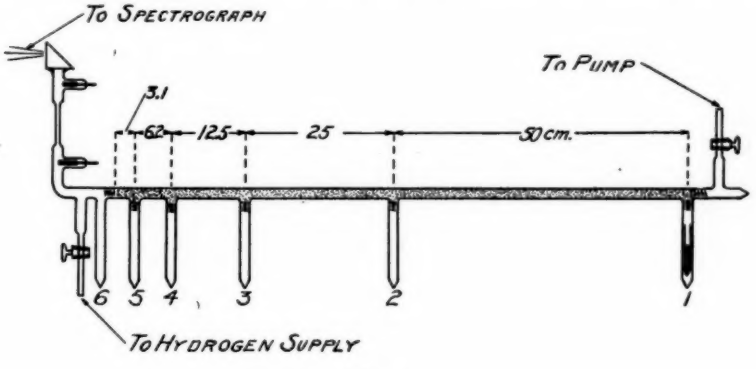

Fig. 1.

somewhat more than a meter in length and a Plücker tube is attached at the end. One branch leads to the pump and a second to the hydrogen supply, this gas being chosen because its low atomic weight makes its

spectrum extremely sensitive to traces of mercury vapor.[1] The remaining six branches are spaced as shown, rather than uniformly, in order that fewer branches with fewer trials will determine the lower limit of length in case it should be small. The Plücker tube is equipped with aluminum electrodes sealed in with platinum wire and is closed with a small right-angled quartz prism instead of plate, that it may be placed between the spectrograph slit and the end of another tube already lined up and which it was desired should not be disturbed.

The chips are closely packed, without jamming, for a length of 96.8 cm. and the test consists in leaving mercury in successive branches, beginning at the pump end, for certain lengths of time and noting from which branch mercury first appears as an impurity in the spectrum. After the vapor had penetrated from the third branch the remaining

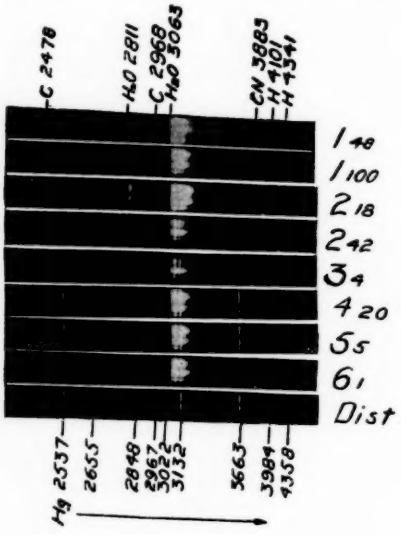

Fig. 2.

branches were also used to see if there were any further increase in strength of the mercury spectrum with time and with decrease of length of packing. To make the test more severe the mercury is kept at a temperature of 120–130 degrees with a small heating coil slipped over the branch, giving vapor pressures of 0.78–1.24 mm.[2]

Electrolytically prepared hydrogen dried with calcium chloride was admitted from time to time and, after adjustment to a suitable pressure indicated by the number of striations between the end of the capillary

[1] Lewis, Astrophysical Journal, 10, 137, 1899, and Nutting, same, 19, 105, 1904.

[2] Hertz, Wied. Ann., 17, 199, 1882.

and one of the electrodes, its spectrum was examined both visually and photographically. The voltage on the exciting transformer, capacity, length of spark gap and time of exposure were all constant. Nine of the spectrograms appear in Fig. 2, where the numbers at the right refer to the branch containing the mercury and the subscripts to the number of hours it had been there. The two stronger hydrogen lines H_α and H_β could always be seen in the direct vision spectroscope, but the line H_γ is seen only in the first four spectrograms. After that it is suppressed by the mercury which begins to enter from branch 3. The repeated filling with hydrogen is seen to remove all of the carbon and cyanogen and a part of the water vapor present as impurities before spectrogram 1–100 is taken. It is seen that the very persistent line Hg 2537 is present from the start, but that it also is removed on several fillings with hydrogen until in spectrogram 2–42 it is all but visible. In the next, 3–4, where the length of intervening packing is only 21.8 cm. the line again appears, showing that the vapor is able to penetrate from the third branch. The next three exposures show no progressive increase in intensity of the many mercury lines with time. The last spectrogram was taken after mercury had been distilled from the last branch to the vicinity of the electrode.

The results may be summed up in the statement: A column of chips of tin-cadmium alloy, which need not be more than 50 cm. in length, is an effective bar to the passage of mercury vapor from the pump to the vessel to be exhausted.

PHYSICAL LABORATORY,
UNIVERSITY OF CALIFORNIA,
June 9, 1917.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

EXPERIMENTAL EVIDENCE FOR THE PARSON MAGNETON.

BY L. O. GRONDAHL.[1]

THE Parson Magneton is an electron endowed with a magnetic moment. This moment is estimated as being equal to 3.5×10^{-19} E.M.U. Such an electron would be affected by a non-uniform magnetic field. A conductor placed in such a field would therefore gain a negative potential in that part which lies in the stronger portion of the field. The magnetons would move into the stronger part of the field until equilibrium is established between the magnetic and the electrostatic forces on the magnetons. The potential so established in a conductor connected to earth and placed in a field of 1,000 gausses would be 2.2×10^{-4} volts. This could be measured by an electrometer.

A similar piece of evidence for the existence of the magneton is found in a phenomenon with which the writer has done some work, namely, the effect of a magnetic field on the thermoelectromotive force of magnetic substances.

If, for instance, a copper-iron couple is placed in a magnetic field, its E.M.F. changes. This change, for which at present there does not seem to be a satisfactory explanation, may be very simply explained in terms of the Parson magneton.

Take a copper iron couple, the iron member of which is a short wire which may be placed in a coil. If, while one junction is at 0° C., the other at 100° C., a current is turned on in the coil, there will be in general a stronger magnetic field in the copper attached to the cold junction than in that attached to the hot junction. At both junctions there will be an increase in magneton concentration in the copper due to the magnetic field. The increase in concentration will, however, be greater at the cold junction, and if we accept this explanation for thermal electromotive forces, this, since iron is positive with reference to copper, means an increase in the thermal E.M.F.

Qualitatively this is in agreement with experimental facts as shown by Fig. 1. This is taken from an earlier paper. The ordinates represent change

[1] Abstract of a paper presented at the meeting of the American Physical Society, December 27–30, 1917.

in E.M.F., the abscissæ the strength of the field in which the iron is placed It will be noticed that in the case of the iron we do get an increase in thermo-electromotive force for all but the very low fields. It will be remembered, however, that at low fields the permeability changes with temperature in the opposite way, so the reverse effect would be expected. Nickel and cobalt are negative with reference to copper, so the effect results in a decrease of the electromotive force. There should be a reversal here, as well, since the permeability varies in the same way. This is, however, not shown by the

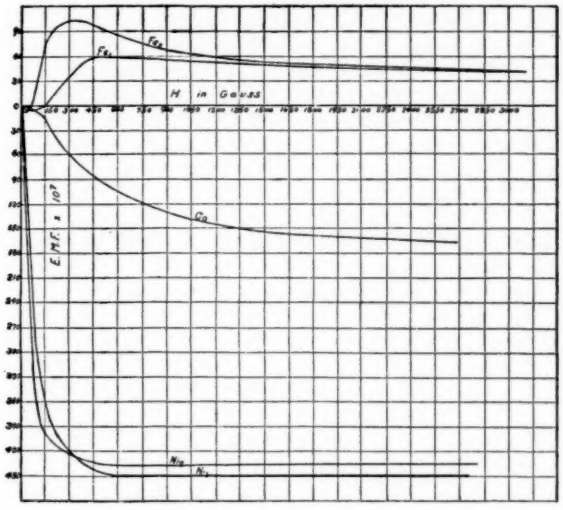

Fig. 1.

experimental results. These effects are so small that a reversal at low fields might easily escape detection.

The quantitative relation is not exactly determined by experimental data in existence at present. That it is of the right order of magnitude, however, may be shown by the following: The change in permeability for iron in a field of 100 gausses between 0° and 100° C. is of the order of magnitude .7, one specimen given in the Smithsonian tables changing from 177.9 at 0° C. to 177.2 at 100° C. The potential established by the field is $H \times 2.2 \times 10^{-7}$ volts. The difference in field intensity at the two ends may be something like 30 gausses. Then the effect on the electromotive force would be 66×10^{-7} volts. One specimen gives about 30, the other about 90×10^{-7}. In order to expect a better check it would be necessary, of course, to determine both quantities in the same specimen. It may be that the effect of the field variation in the magnetic member should be included in the calculation. This would make the result larger.

The specimen of nickel also recorded in the Smithsonian tables, has a permeability at 0° C. of 1.6, at 100° C. of 1.5, with a field strength of 12,000

gausses. By the same method of calculation this will give a change in E.M.F. due to the field of 600×10^{-7} volts. Experiment gives as a maximum for two specimens of nickel that were tried 450×10^{-7} volts. In the case of cobalt, a similar calculation gives for a specimen recorded by Stifler in the PHYSICAL REVIEW, 49×10^{-7} while for a specimen given in the Smithsonian tables they get 96×10^{-7}. The specimen on which the experiment was tried gave, approximately, 160×10^{-7} volts.

These calculations are all necessarily very rough, but nevertheless show a fair quantitative agreement. In some experiments that are under way for another purpose, the writer hopes to get the data necessary for a more accurate determination of this quantitative relation. This explanation would involve as a corollary that the copper would become magnetized due to the orientation of the free magnetons. Assuming that the magnetons can be oriented and that they would distribute themselves in all possible angles according to the same law that Langevin assumed for paramagnetic substances, and assuming that the number of free magnetons is the same as that usually assumed for the number of free electrons in copper, it may be shown that for a field strength of 9,000 gausses the intensity of magnetization of copper would be approximately 270. This may be masked by diamagnetism.

CARNEGIE INSTITUTE OF TECHNOLOGY,
January, 1917.

NEW BOOKS.

La Chimie des Elements Radioactifs. By F. SODDY. Paris, Librairie Gauthier. Villars, 1916. Pp. iv + 174. Price, 5 fr.

This is an excellent translation of Soddy's book, both parts being contained in one volume. An improvement on the original has been made by putting references in footnotes instead of at the end of the volume. As in the original, an index for the second part is lacking.

E. P. L.

Groupes Electrogenes en regime trouble. By L. BARBILLION. Paris, Gauthier-Villars, 1915. Pp. ii + 306. Price, 11 fr.

This book is based on a course of lectures given in the Electrotechnical Institute of the University of Grenoble. Its publication was delayed on account of the fact that the author reported for military duty on the first day of the war. It discusses from the theoretical standpoint the perturbations of prime movers of all kinds and of direct and alternating current generators, due to variations of velocity or of load, and the different methods of regulation. Both analytical and graphical methods are employed, many of the latter original. Characteristic gallic clearness of presentation and unusually good typography combine to make this a very attractive volume.

E. P. L.

Ozone. By A. VOSMAER. New York: D. Van Nostrand Company, 1916. Pp. xii + 197. Price, $2.50.

In the preface of this book, the full title of which is "Ozone, its Manufacture, Properties, and Uses," we are told that the author's "main object was to give a full outline of our personal experience and that same experience has made us very critical about outside information." This emphasis upon his personal experiences and opinions, and distrust of all "outside information" is much in evidence throughout the book. The volume is distinctly technical rather than scientific; while it may be of interest and value to those engaged in the manufacture and use of ozone, the reader, must be alert for loose statements and errors.

N. E. D.

The Dynamical Theory of Gases. By J. H. JEANS. Cambridge: University Press. 1916. Pp. vi + 436. Price, $4.00.

A study of this second edition of Jeans' well-known treatise reveals many improvements over the first edition of thirteen years ago. Much of the book

has been rewritten or rearranged so as to secure a more logical sequence in the presentation. Many of the obvious steps formerly given in the mathematical development have been omitted, thus securing a more concise treatment and assisting the reader in obtaining a bird's eye view of the problem and its solution. The omission of some of the introductory and subsidiary matter found scattered through the former edition likewise aids the reader. A number of the tables have been greatly changed, some have been recomputed, others have been based upon other authorities, some have been omitted, all give evidence of a more careful selection of material. There is a noticeable decrease in the number of references to and quotations of data from similar treatises and a corresponding increase in the number of references to and of data derived from original sources. An increase in the number of subheadings increases the value of the volume as a book of reference. Much new matter has been added; the former edition contained 420 numbered sections and 777 numbered equations, the present edition contains 559 sections and 1044 equations.

The plan of the book is thus set forth by the author: "My primary aim in the first edition of this book was to develop the Theory of Gases upon as exact a mathematical basis as possible. This aim has not been forgotten in the preparation of a second edition, but has been combined with an attempt to make as much of the book as possible intelligible to the non-mathematical reader. I have adopted the plan, partially followed in the first edition, of dividing the book to a large extent into mathematical and physical chapters." In taking up a new book treating of the Dynamical Theory of Gases one at once looks to see what prominence the author has given to the Quantum Theory and in what manner he has introduced it. Jeans has "confined the Quantum Theory to the last chapter; the difficulties arising out of the classical treatment have been allowed to emerge in the earlier chapters, but have been left unsolved. The last chapter merely indicates how these difficulties disappear in the light of the new conceptions of the Quantum Theory; no attempt is made to give a full or balanced view of the whole theory." The volume will be a valued addition to the library of any one interested in the study of the dynamical theory of gases.

N. E. D.